#6

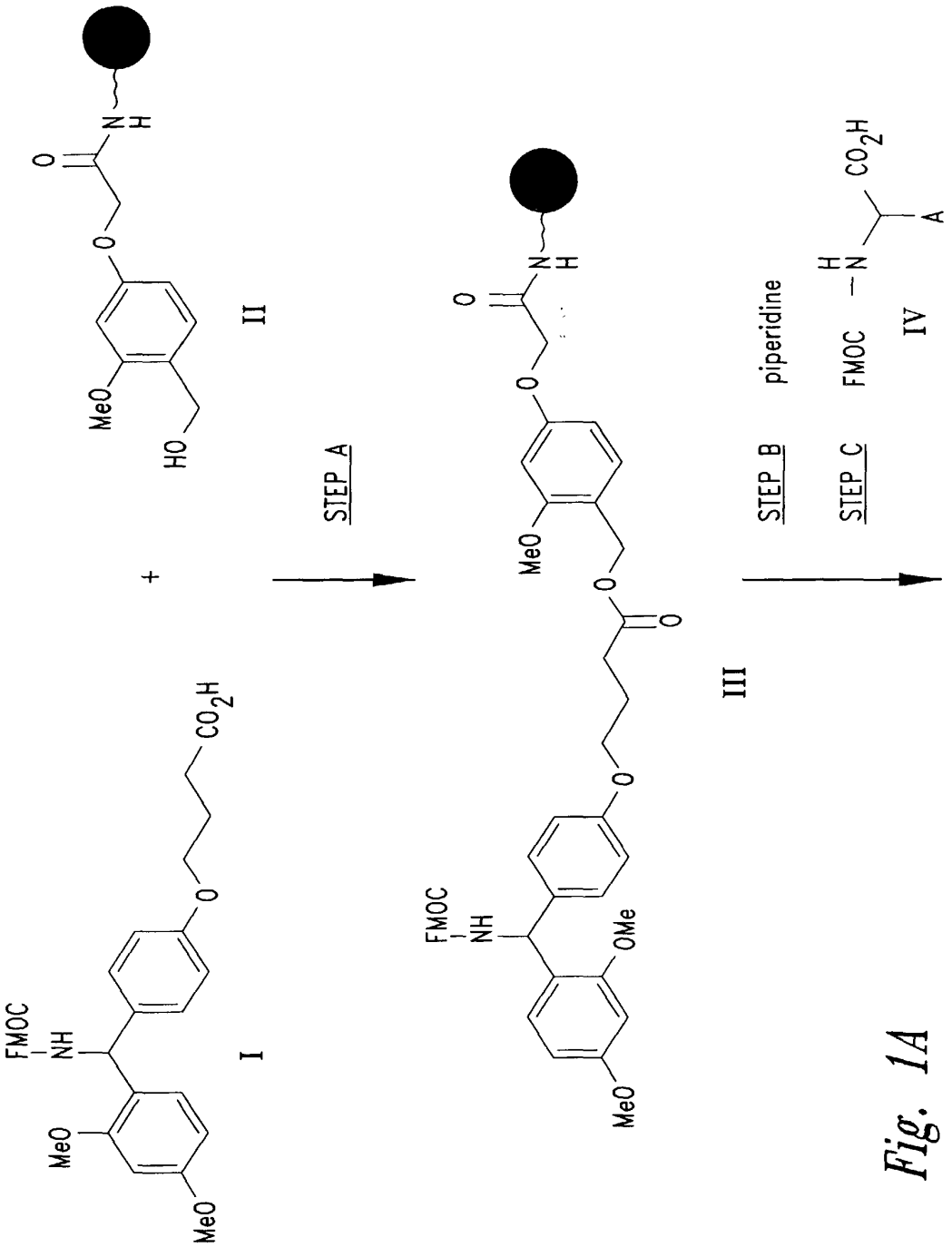


Fig. 1A

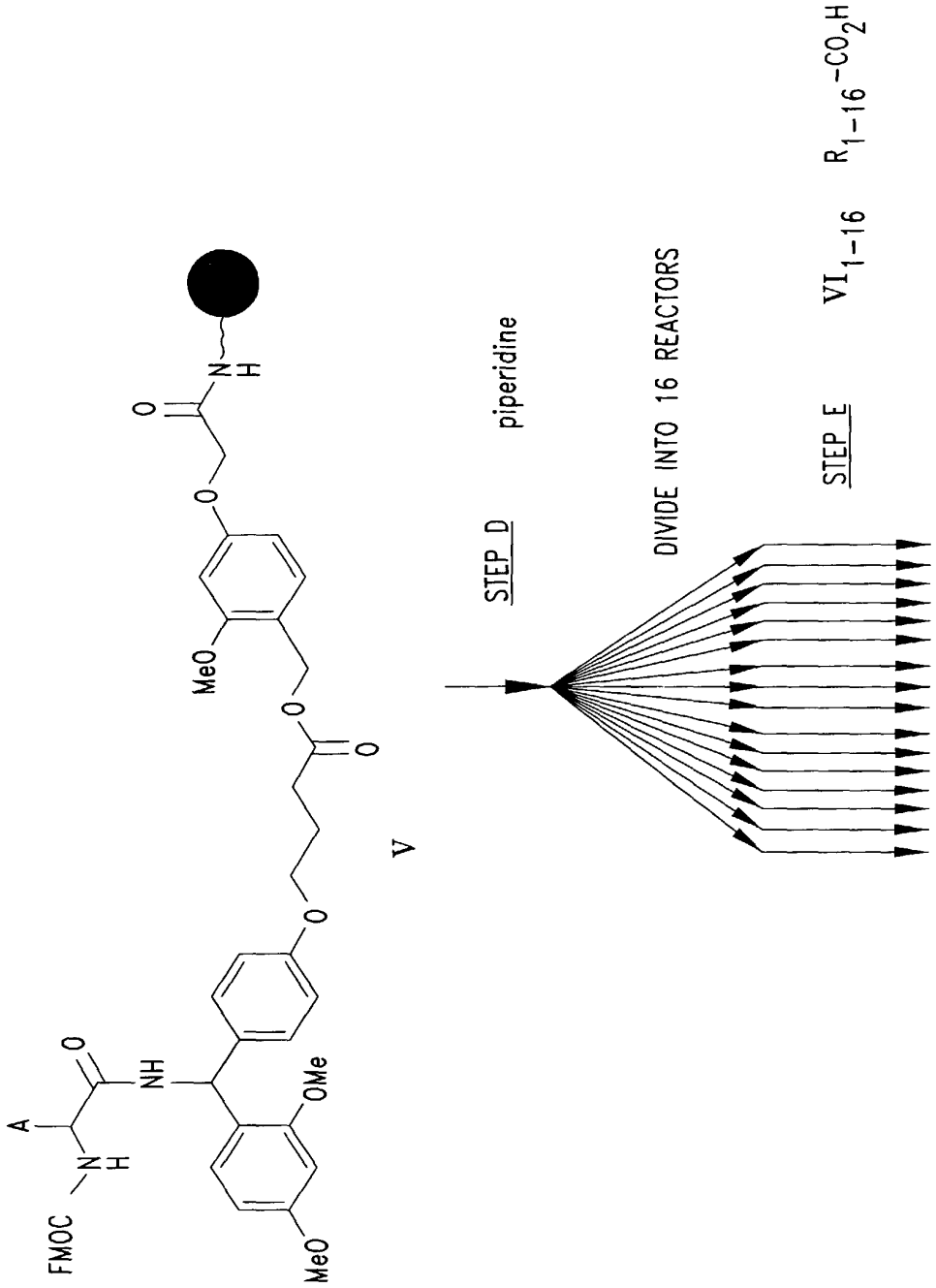

V
STEP D
piperidine
DIVIDE INTO 16 REACTORS
STEP E
VI_{1-16}
$R_{1-16}-CO_2H$
FMOC
A
NH
OMe
MeO
MeO

Fig. 1B

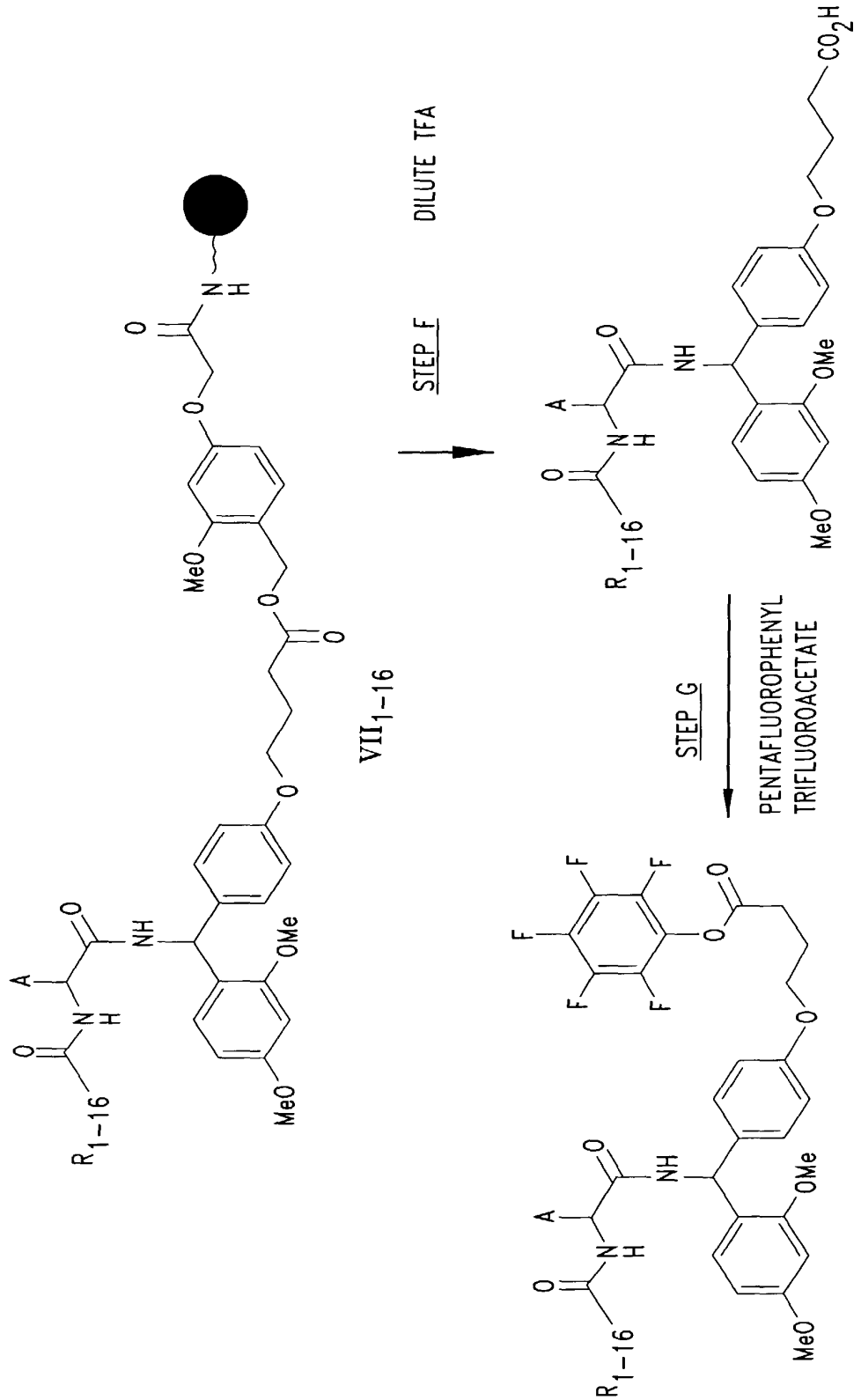

DILUTE TFA
STEP F
STEP G
PENTAFLUOROPHENYL
TRIFLUOROACETATE
VII1-16
VIII1-16

Fig. 1C

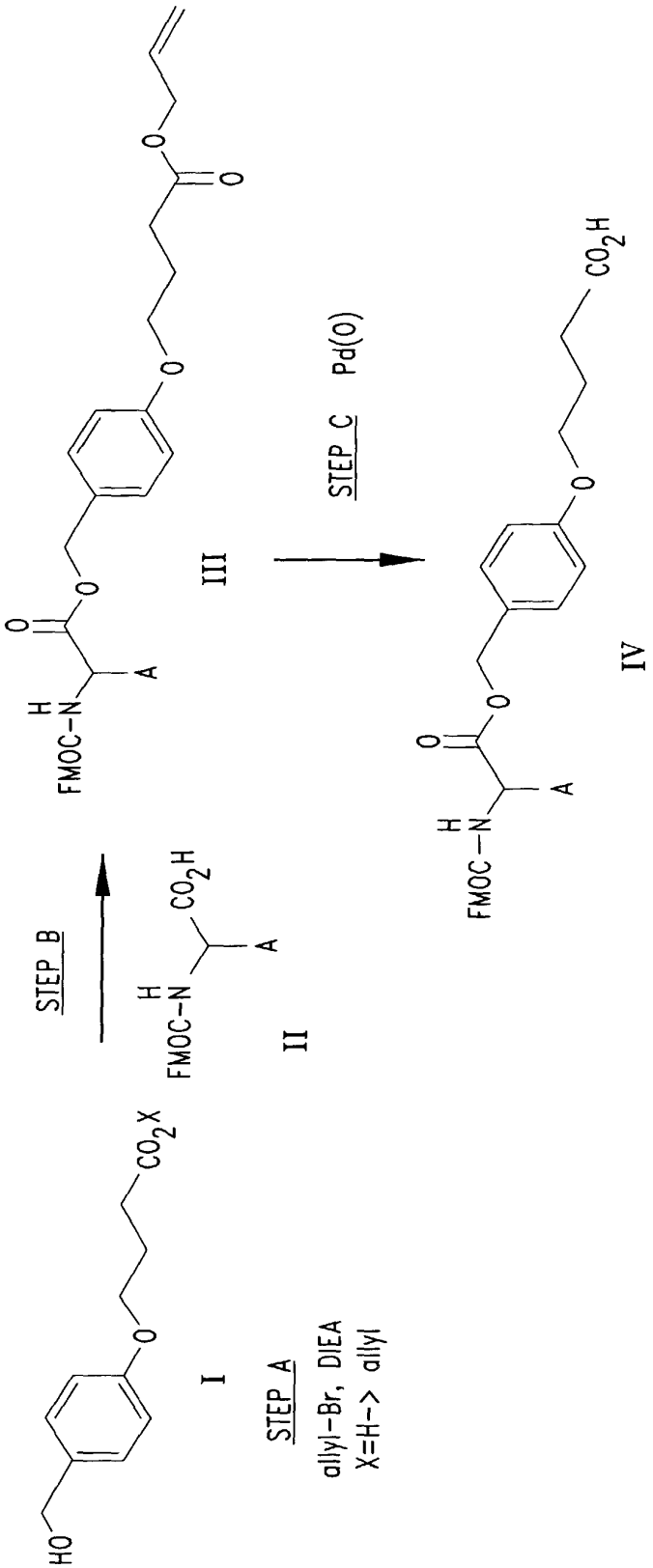

HO
CO_2X
I
STEP A
allyl-Br, DIEA
X=H-> allyl
FMOC-N
H
A
CO_2H
II
STEP B
III
STEP C Pd(0)
IV
O

Fig. 2A

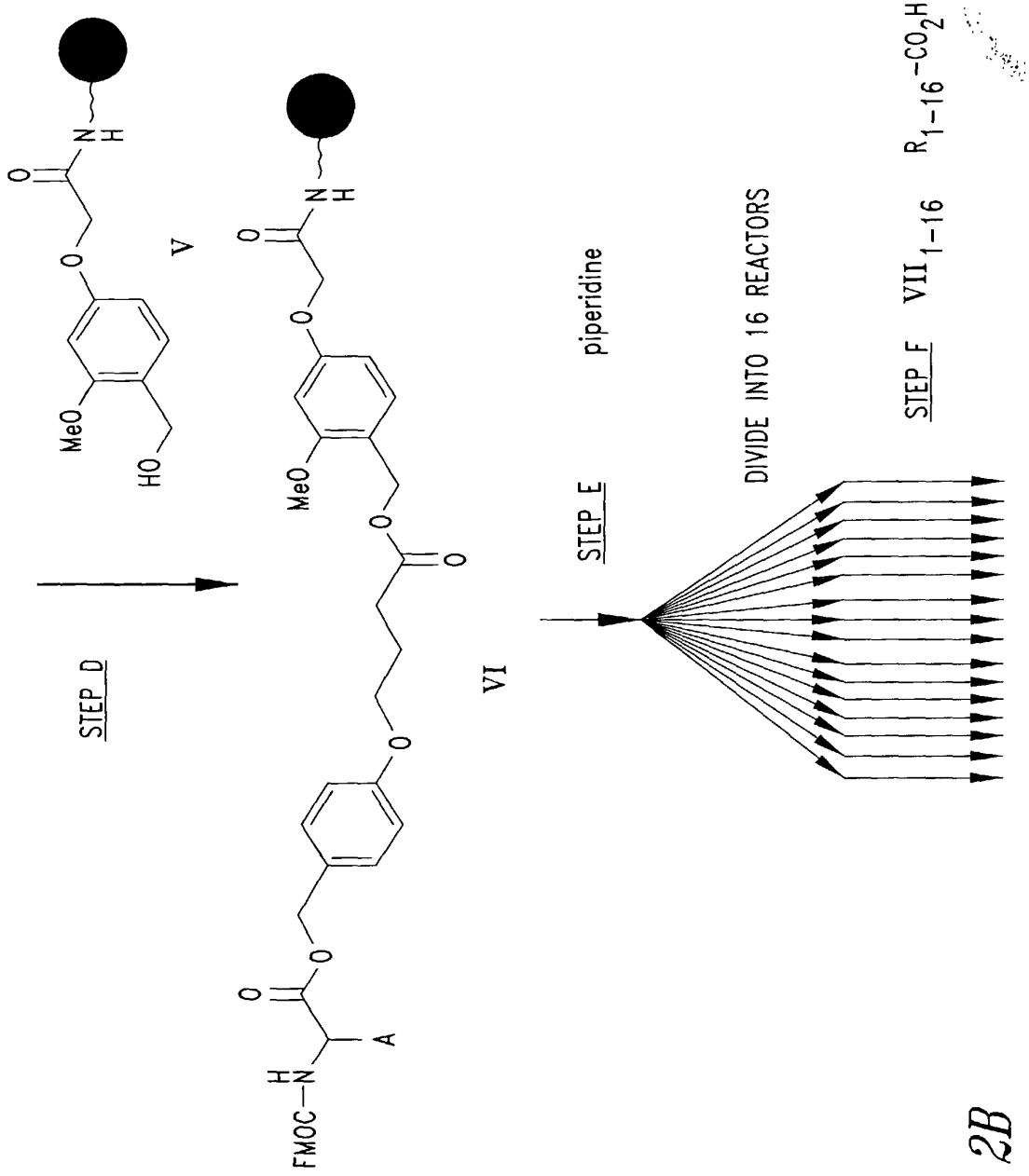

V
VI
STEP D
STEP E
piperidine
DIVIDE INTO 16 REACTORS
STEP F
VII 1-16
R1-16-CO2H
MeO
HO
FMOC—N
H
A

Fig. 2B

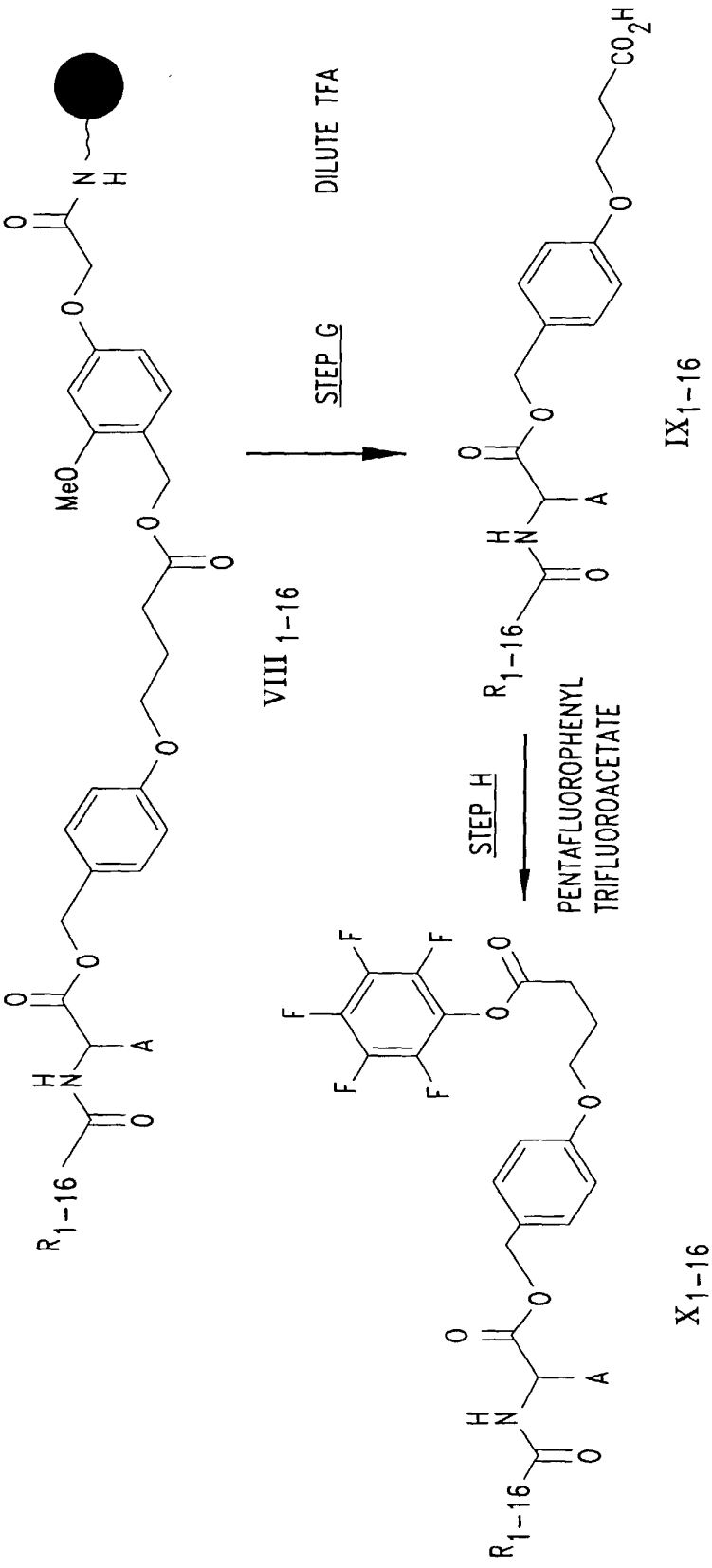

DILUTE TFA
STEP G
STEP H
PENTAFLUOROPHENYL
TRIFLUOROACETATE
MeO
VIII 1-16
IX 1-16
X 1-16
R 1-16
A

Fig. 2C

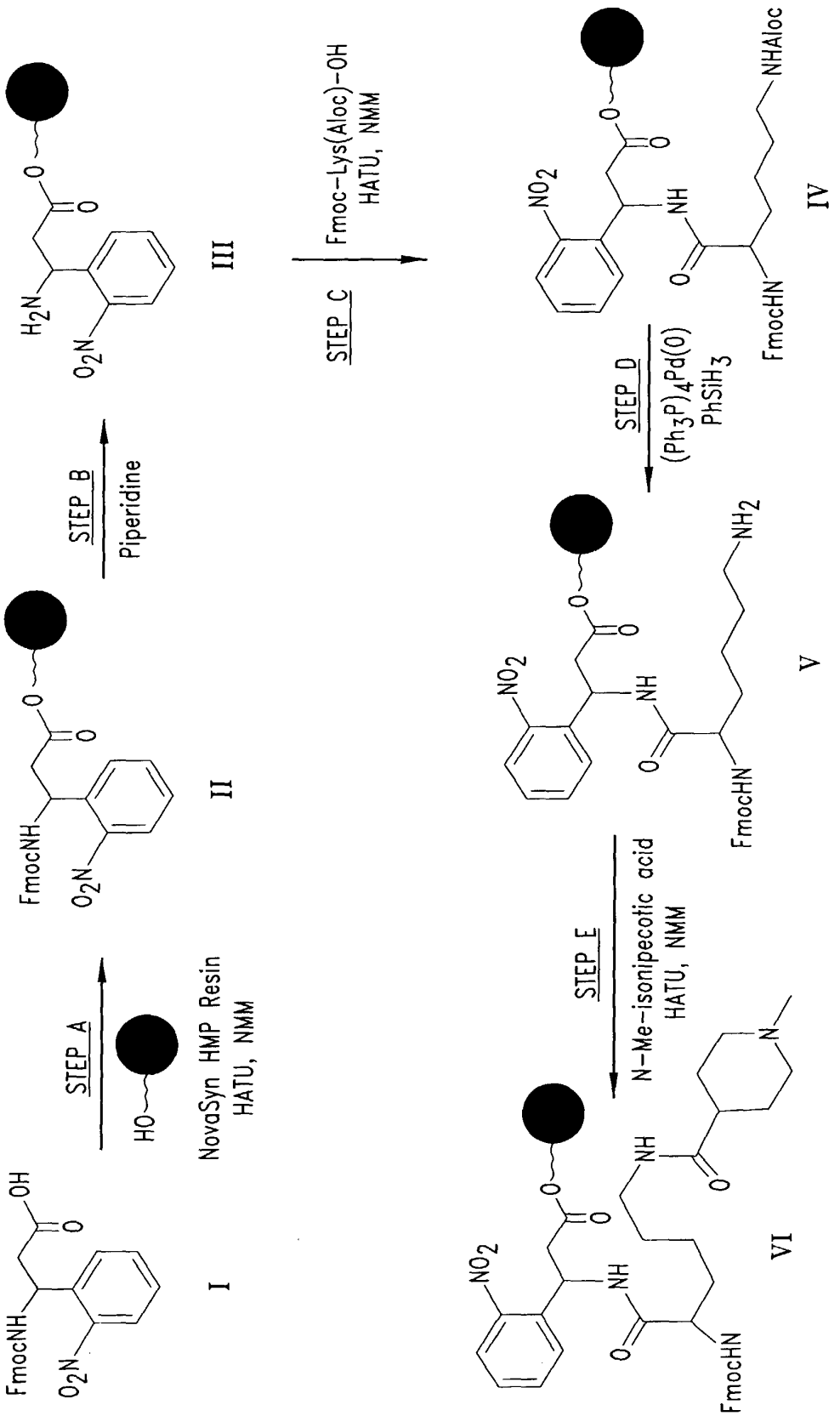

STEP A
NovaSyn HMP Resin
HATU, NMM
STEP B
Piperidine
STEP C
Fmoc-Lys(Aloc)-OH
HATU, NMM
STEP D
$(Ph_3P)_4Pd(0)$
$PhSiH_3$
STEP E
N-Me-isonipecotic acid
HATU, NMM
I
II
III
IV
V
VI

Fig. 3A

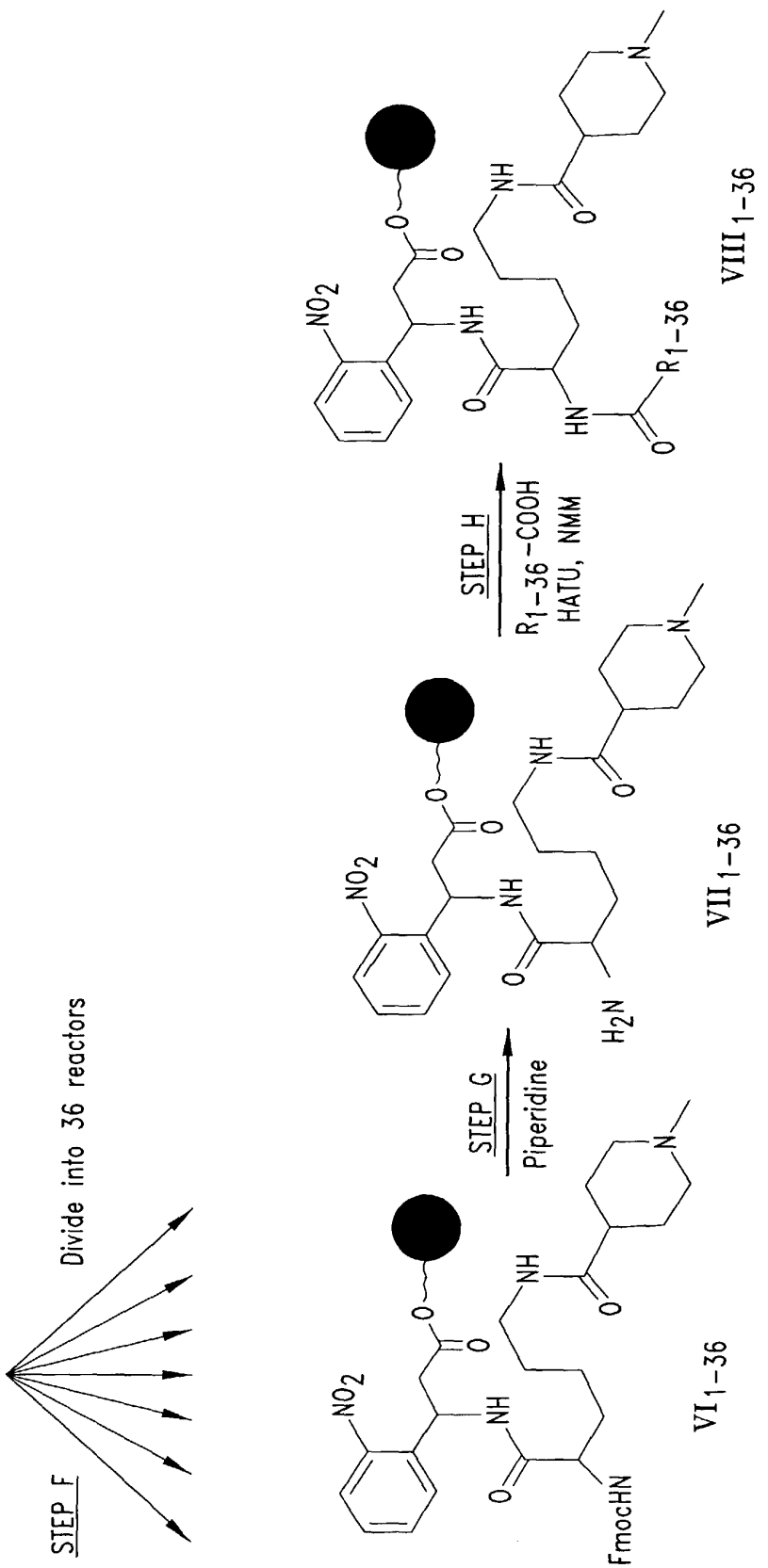

STEP F
Divide into 36 reactors
VI 1-36
FmocHN
STEP G
Piperidine
VII 1-36
H2N
STEP H
R1-36-COOH
HATU, NMM
VIII 1-36
NO2
NH
O
N
R1-36
HN

Fig. 3B

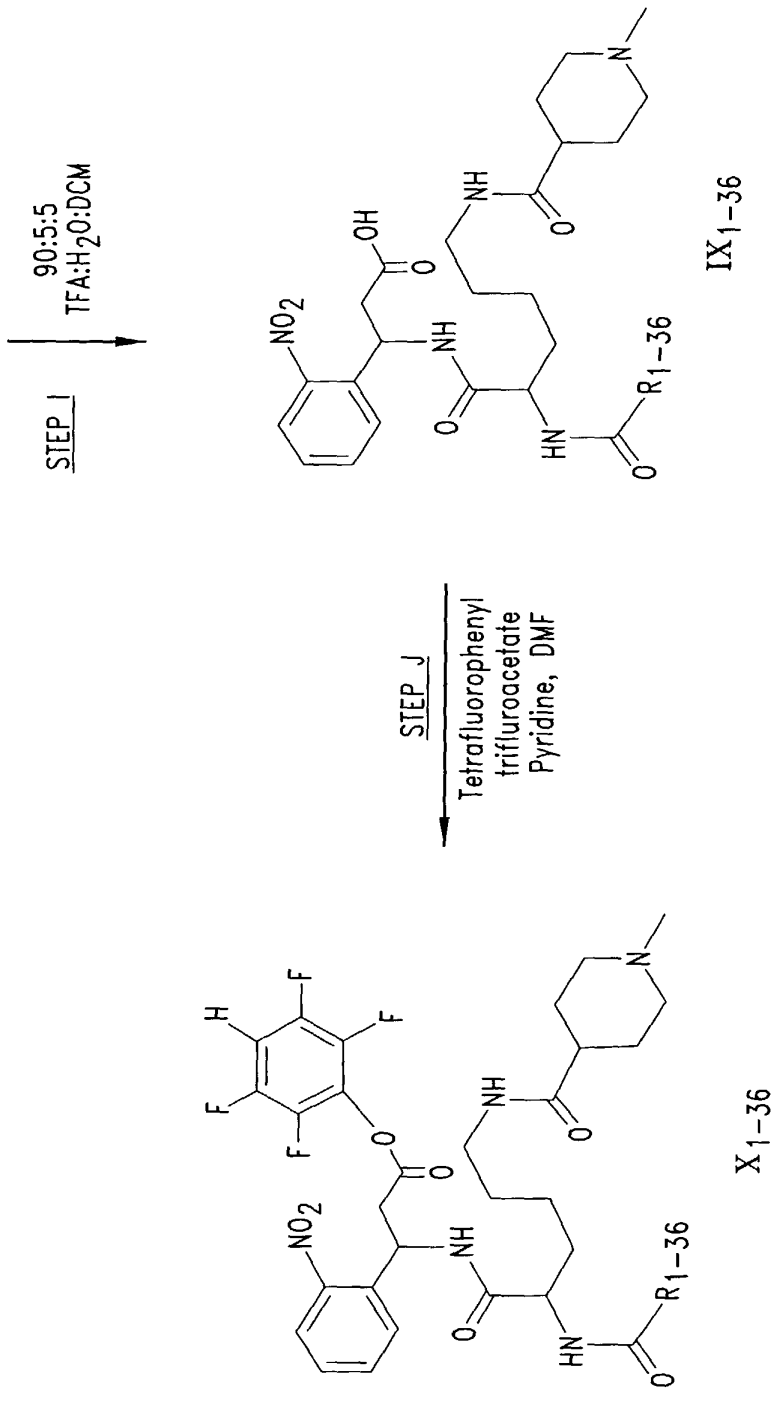

STEP I
90:5:5
TFA:H2O:DCM
IX1-36
STEP J
Tetrafluorophenyl
trifluroacetate
Pyridine, DMF
X1-36

Fig. 3C

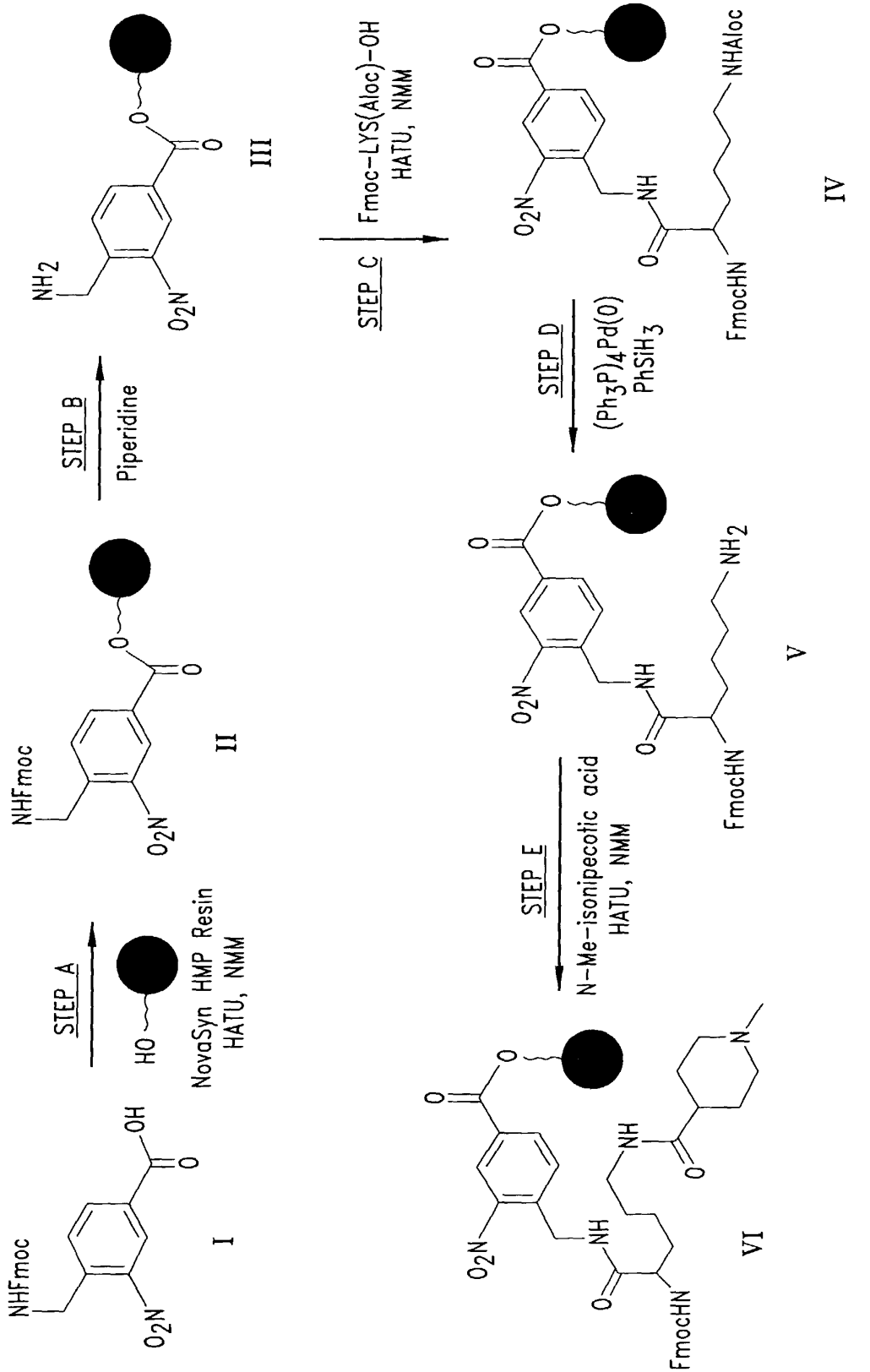

NHFmoc
O_2N
OH
O
I
STEP A
HO
NovaSyn HMP Resin
HATU, NMM
II
STEP B
Piperidine
NH_2
III
STEP C
Fmoc-LYS(Aloc)-OH
HATU, NMM
NHAloc
NH
FmocHN
IV
STEP D
$(Ph_3P)_4Pd(0)$
$PhSiH_3$
NH_2
V
STEP E
N-Me-isonipecotic acid
HATU, NMM
VI

Fig. 4A

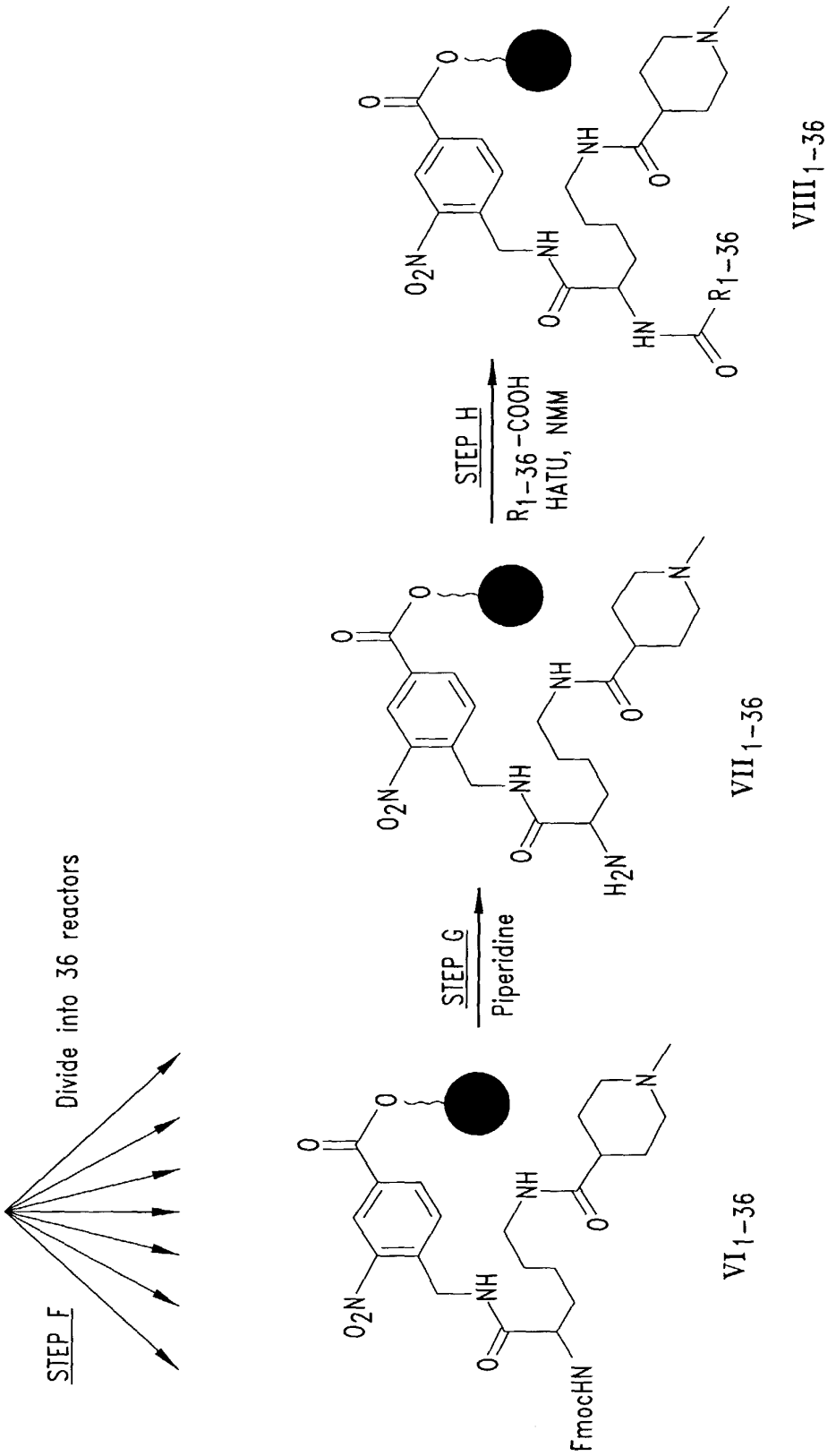

STEP F
Divide into 36 reactors
FmocHN
VI1-36
STEP G
Piperidine
VII1-36
STEP H
R1-36-COOH
HATU, NMM
VIII1-36

Fig. 4B

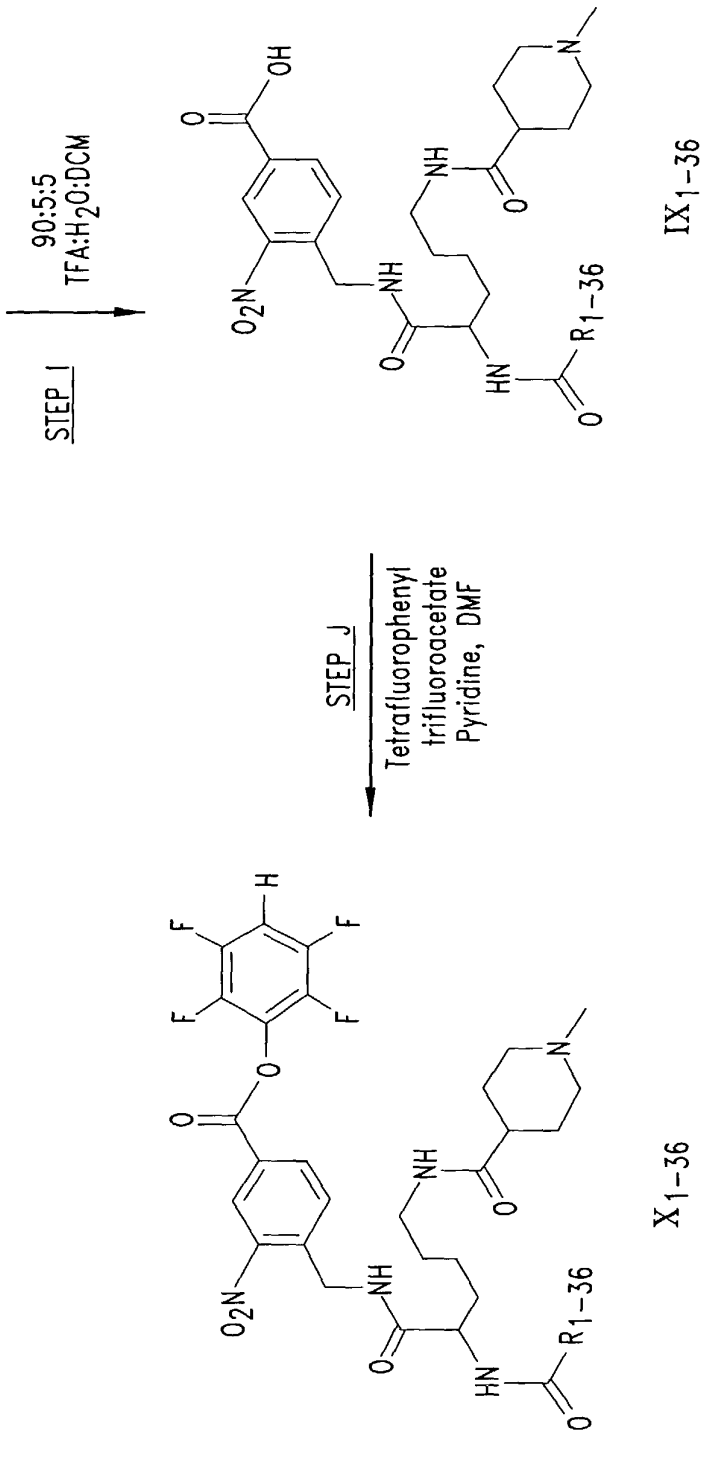

STEP I
90:5:5
TFA:H2O:DCM
IX1-36
STEP J
Tetrafluorophenyl
trifluoroacetate
Pyridine, DMF
X1-36

Fig. 4C

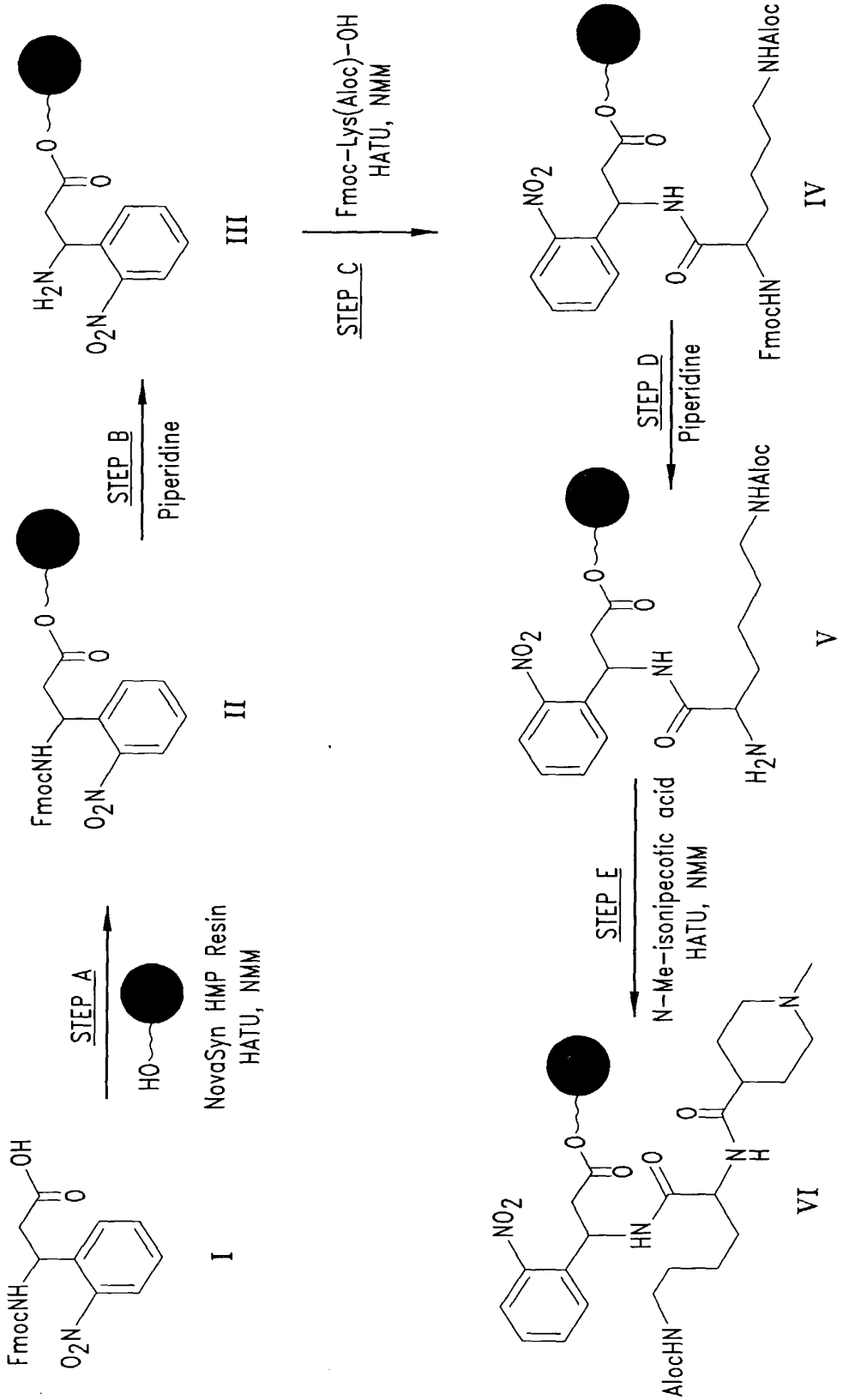

STEP A
HO
NovaSyn HMP Resin
HATU, NMM
I
FmocNH
O2N
OH
STEP B
Piperidine
II
H2N
III
STEP C
Fmoc-Lys(Aloc)-OH
HATU, NMM
NHAloc
FmocHN
IV
STEP D
Piperidine
V
STEP E
N-Me-isonipecotic acid
HATU, NMM
AlocHN
VI

Fig. 5A

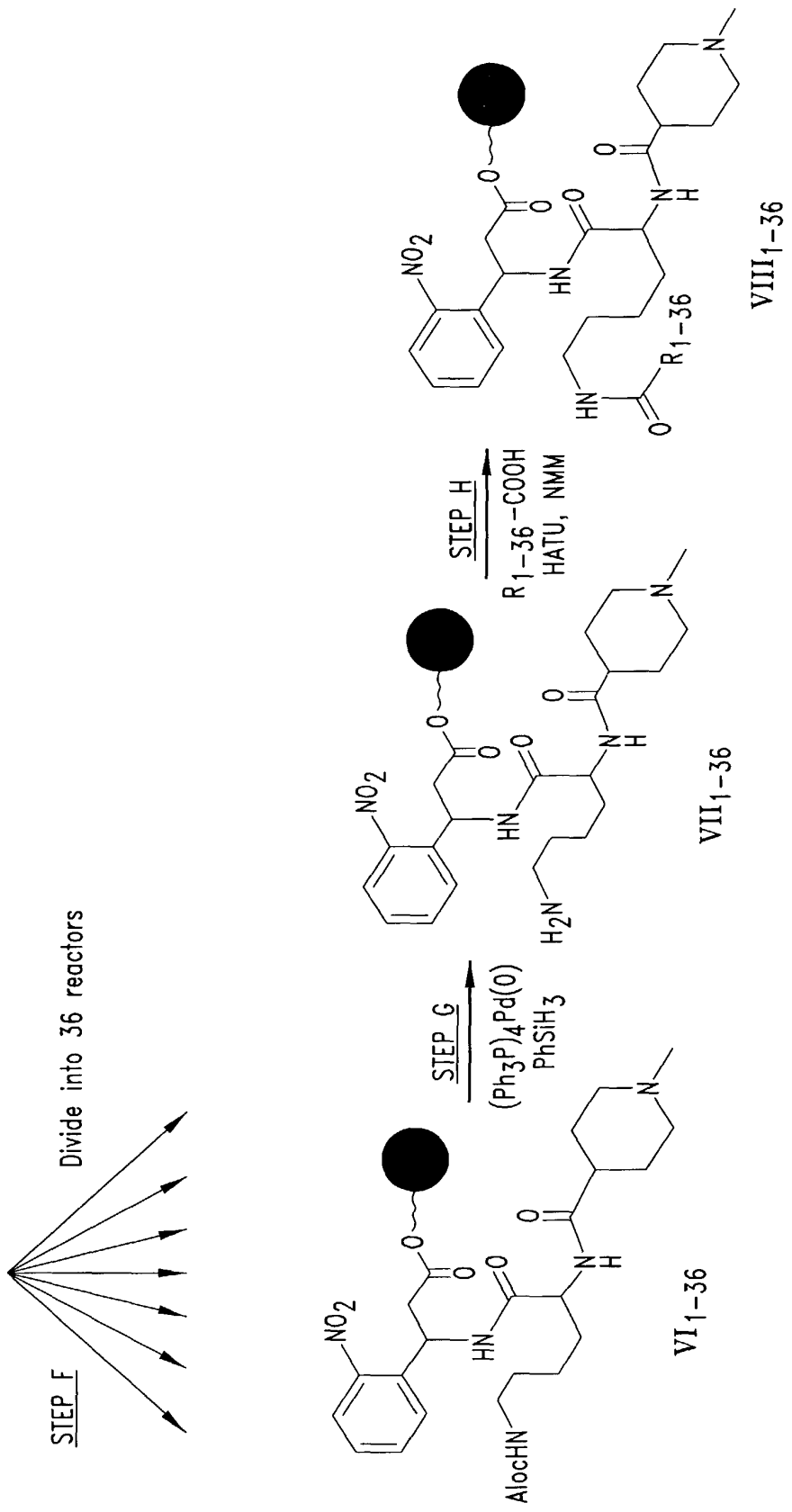

STEP F
Divide into 36 reactors
AlocHN
NO2
HN
O
N
H
VI1-36
STEP G
(Ph3P)4Pd(0)
PhSiH3
H2N
VII1-36
STEP H
R1-36-COOH
HATU, NMM
R1-36
VIII1-36

Fig. 5B

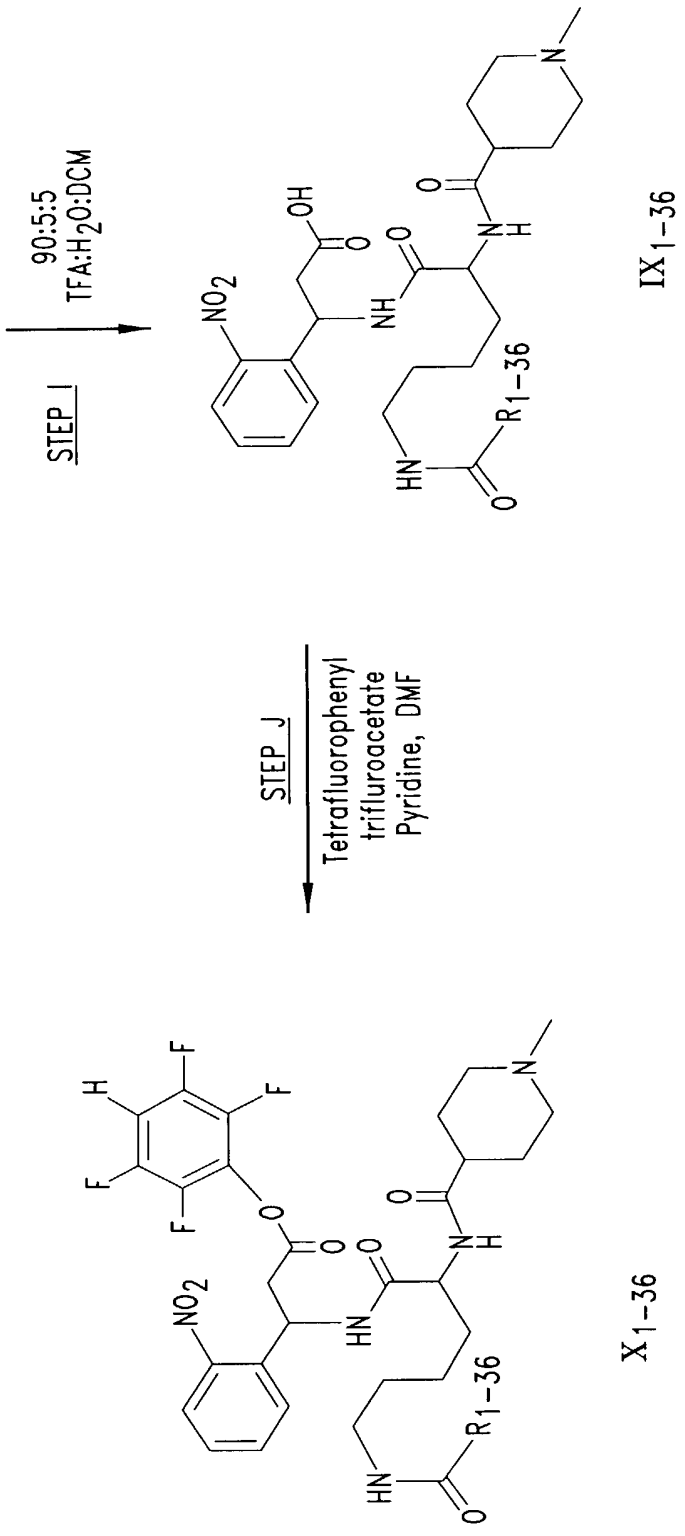

STEP I
90:5:5
TFA:H2O:DCM
IX1-36
STEP J
Tetrafluorophenyl
trifluroacetate
Pyridine, DMF
X1-36

Fig. 5C

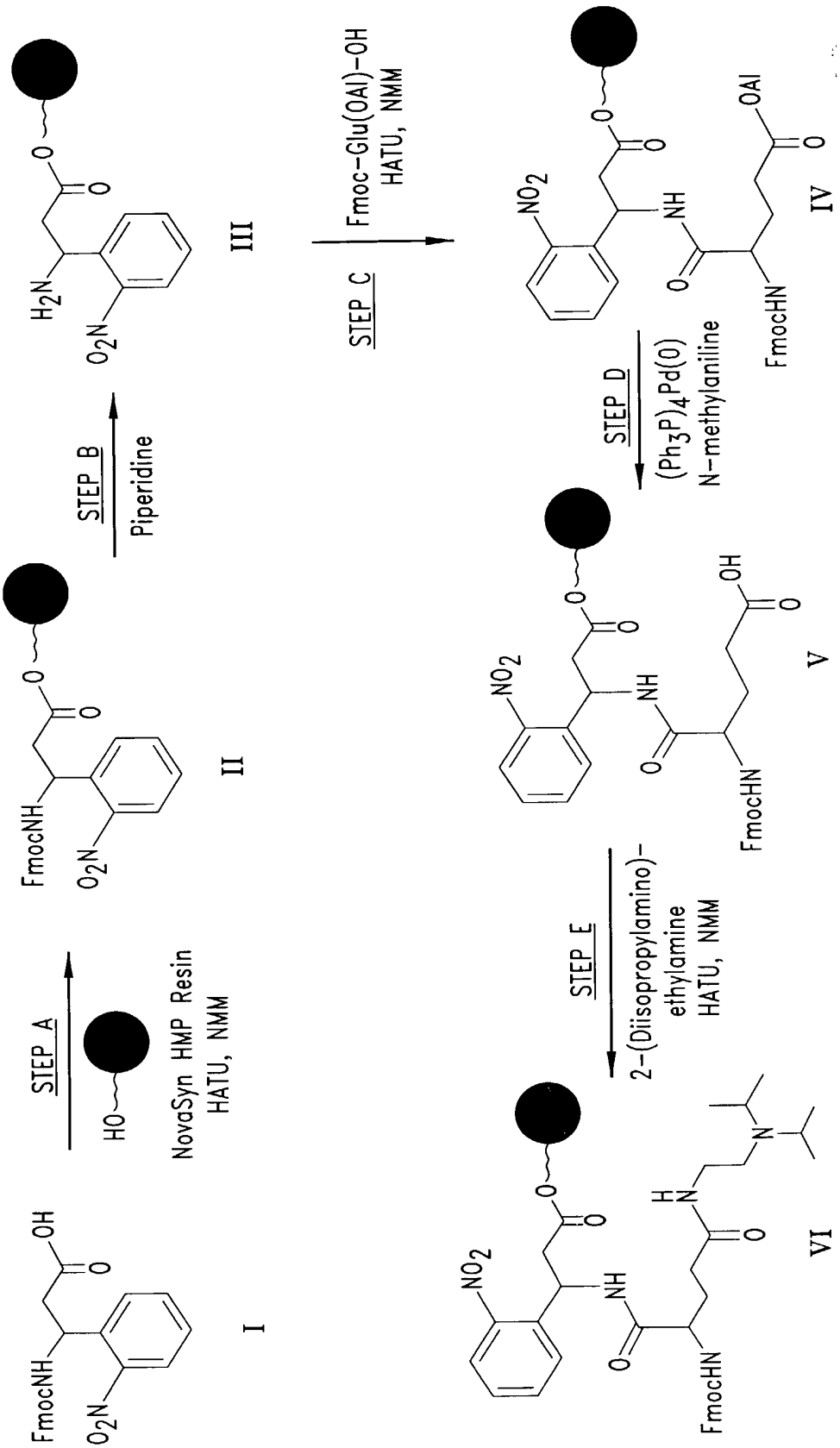

STEP A
NovaSyn HMP Resin
HATU, NMM
STEP B
Piperidine
STEP C
Fmoc-Glu(OAl)-OH
HATU, NMM
STEP D
(Ph3P)4Pd(0)
N-methylaniline
STEP E
2-(Diisopropylamino)-
ethylamine
HATU, NMM
I
II
III
IV
V
VI

Fig. 6A

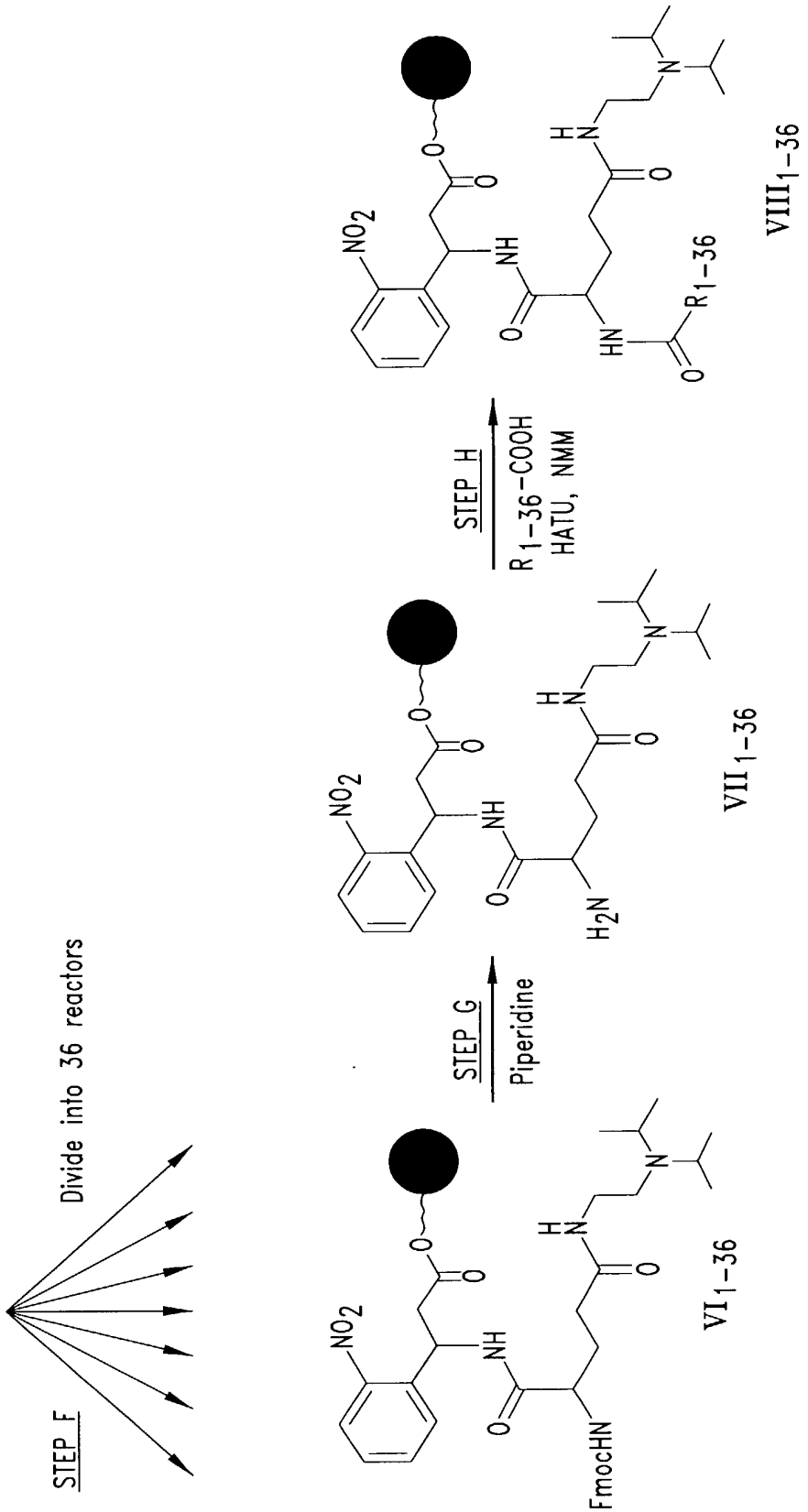

STEP F
Divide into 36 reactors
FmocHN
VI_{1-36}
STEP G
Piperidine
H_2N
VII_{1-36}
STEP H
R_{1-36}-COOH
HATU, NMM
$VIII_{1-36}$

Fig. 6B

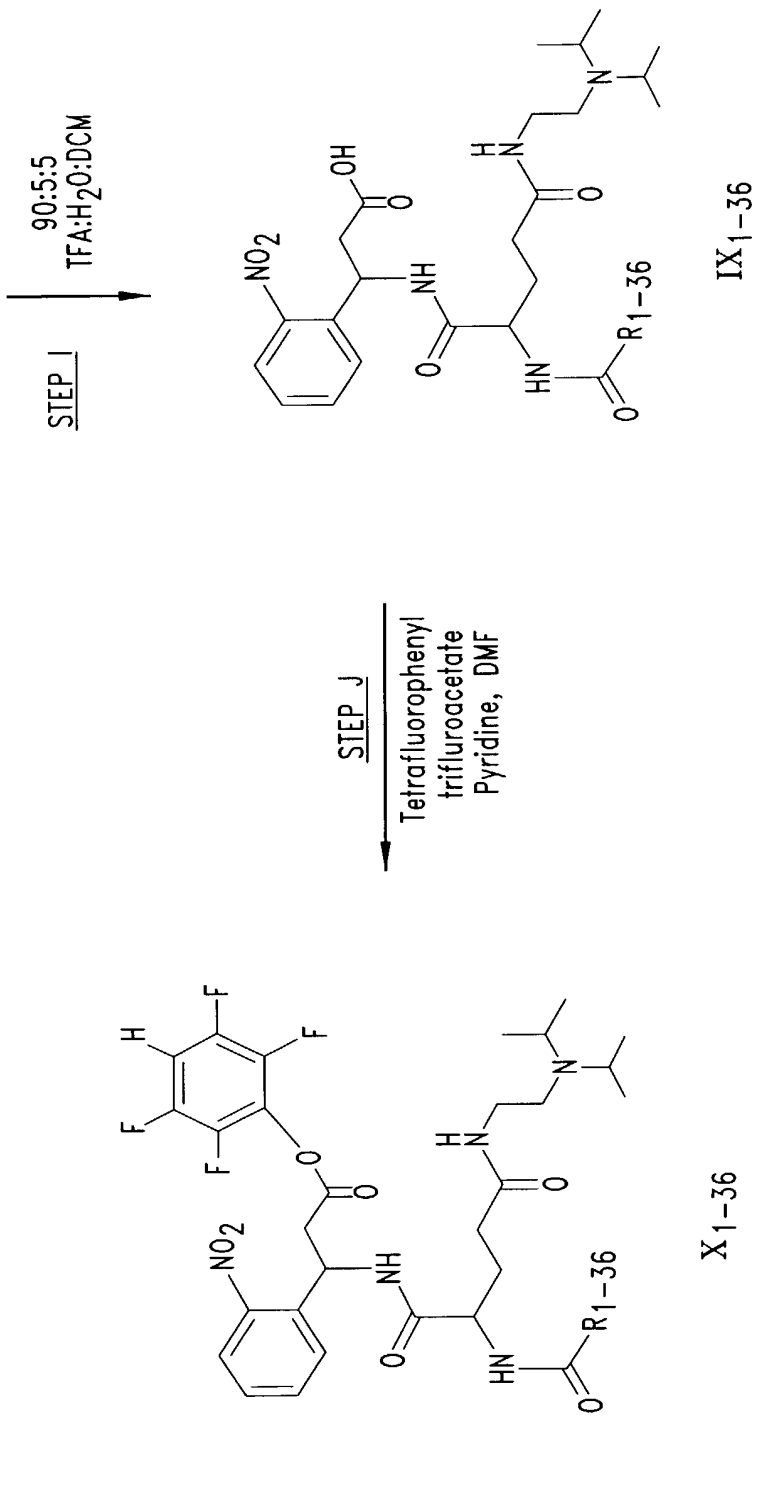

STEP I
90:5:5
TFA:H2O:DCM
IX1-36
STEP J
Tetrafluorophenyl
trifluroacetate
Pyridine, DMF
X1-36

Fig. 6C

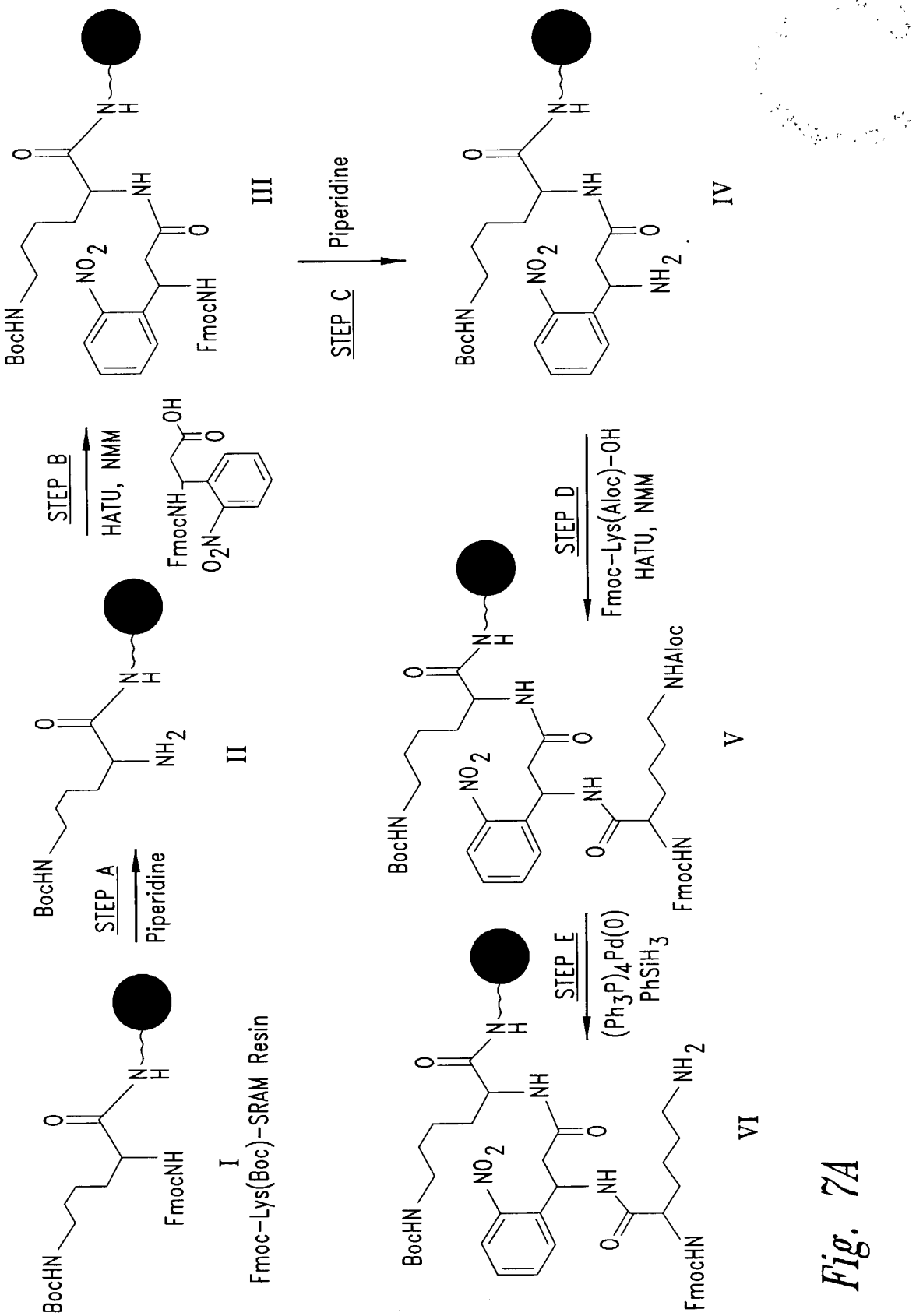

BocHN
FmocNH
NO2
NH2
O2N
OH
NHAloc
FmocHN
STEP A
Piperidine
STEP B
HATU, NMM
STEP C
Piperidine
STEP D
Fmoc-Lys(Aloc)-OH
HATU, NMM
STEP E
(Ph3P)4Pd(0)
PhSiH3
I
Fmoc-Lys(Boc)-SRAM Resin
II
III
IV
V
VI

Fig. 7A

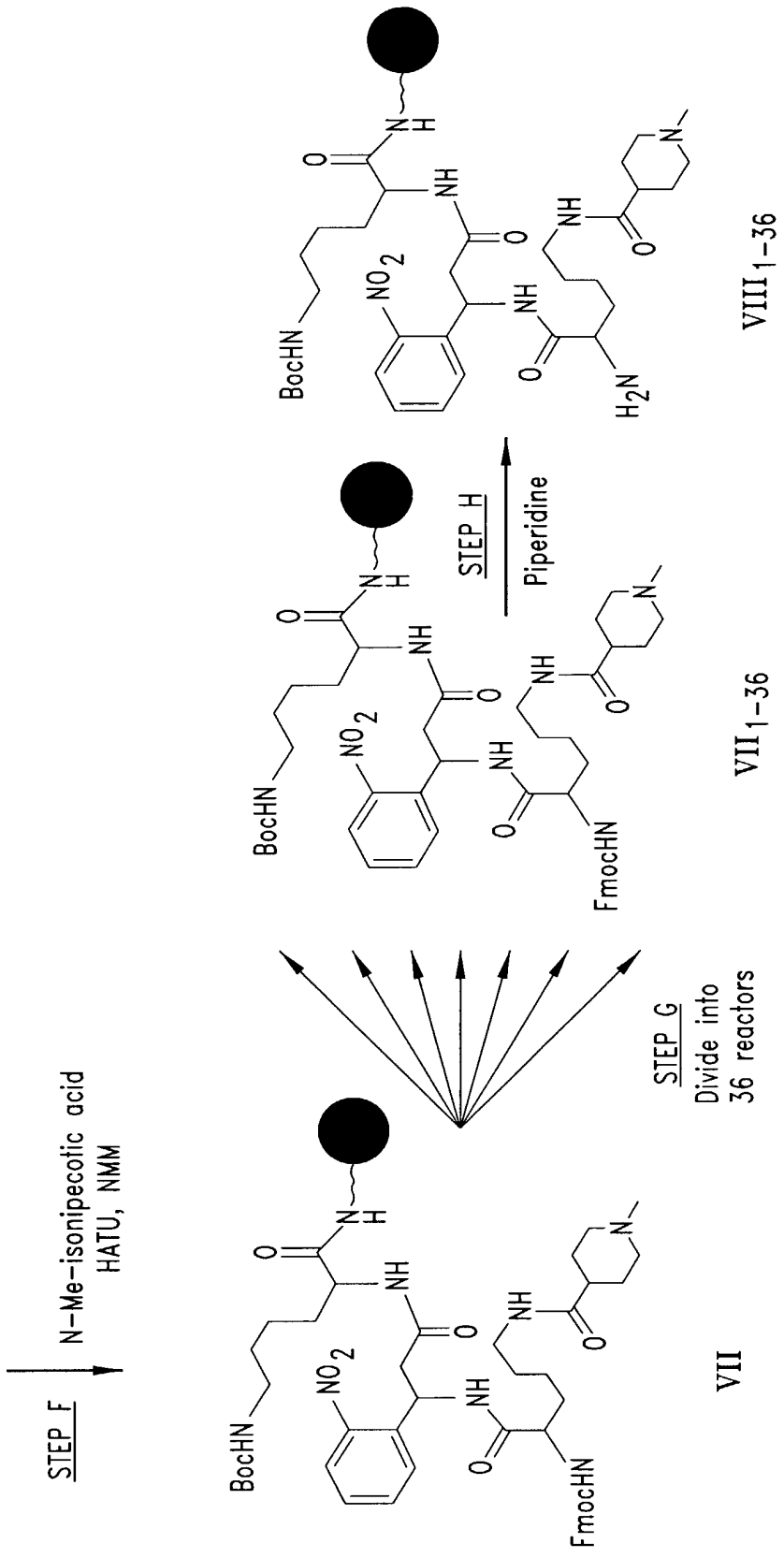

STEP F
N-Me-isonipecotic acid
HATU, NMM
VII
STEP G
Divide into
36 reactors
STEP H
Piperidine
VII1-36
VIII1-36
BocHN
FmocHN
NO2
H2N

Fig. 7B

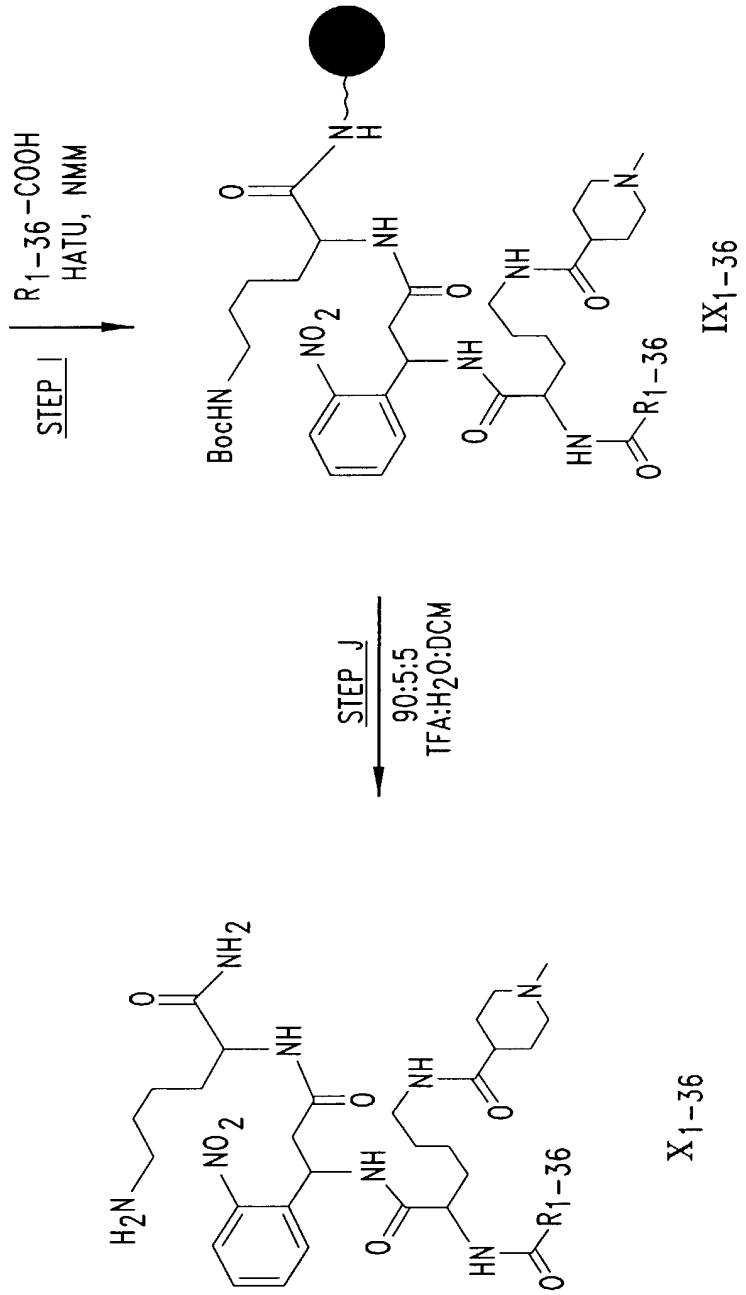

STEP I
R1-36-COOH
HATU, NMM
BocHN
NO2
IX1-36
STEP J
90:5:5
TFA:H2O:DCM
H2N
X1-36

Fig. 7C

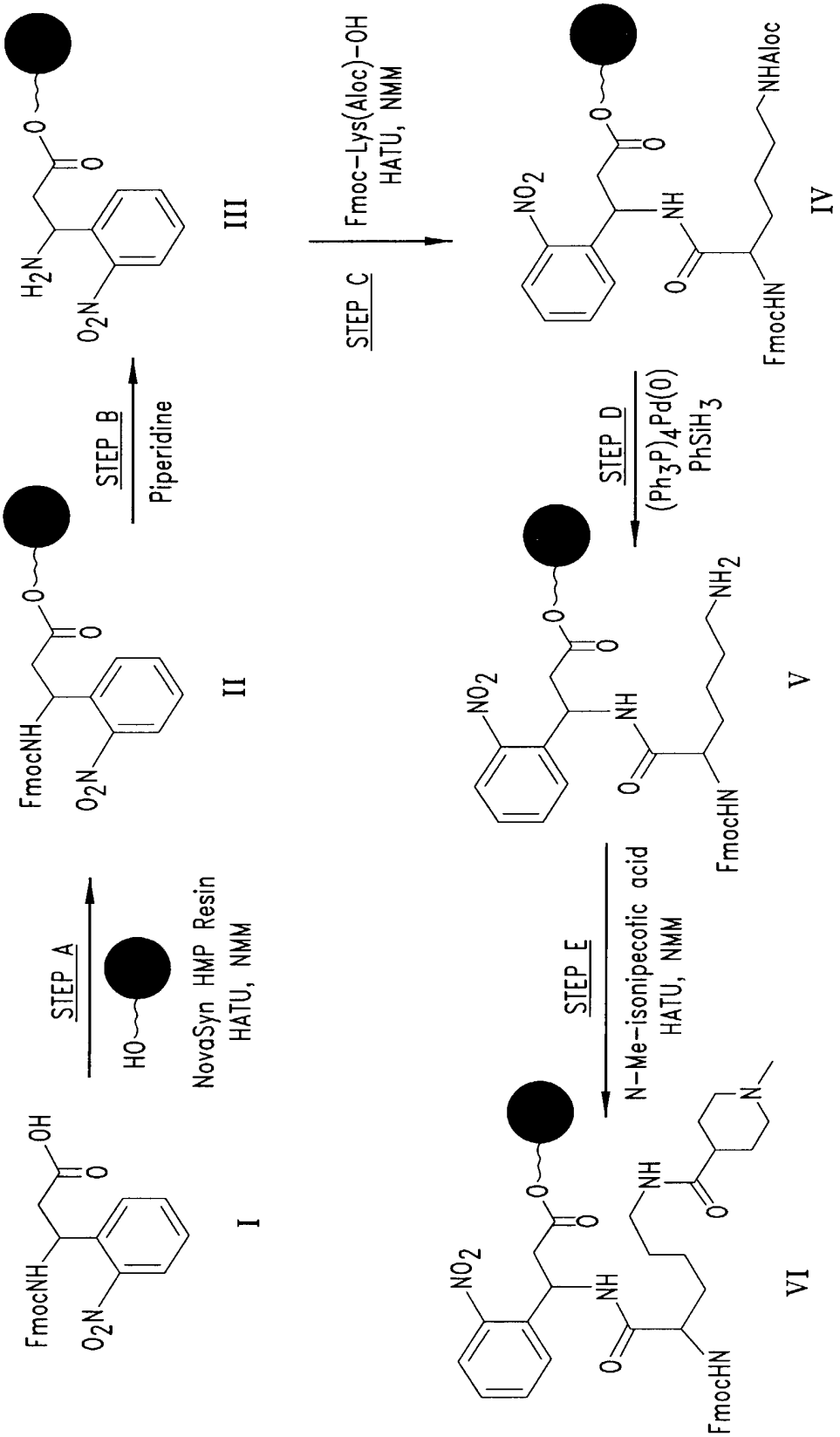

STEP A
NovaSyn HMP Resin
HATU, NMM
STEP B
Piperidine
STEP C
Fmoc-Lys(Aloc)-OH
HATU, NMM
STEP D
(Ph3P)4Pd(0)
PhSiH3
STEP E
N-Me-isonipecotic acid
HATU, NMM
I
II
III
IV
V
VI

Fig. 8A

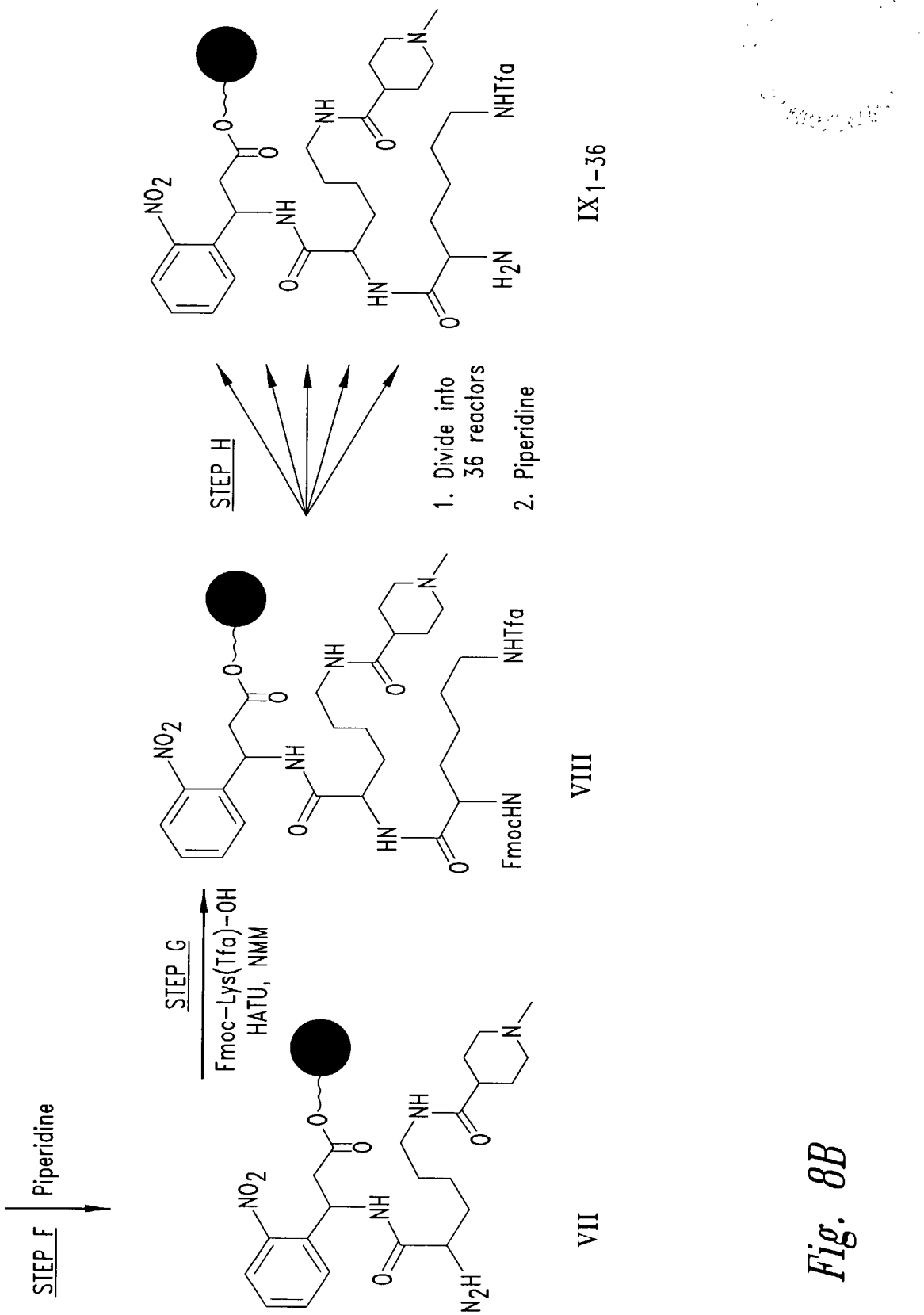

STEP F
Piperidine
VII
STEP G
Fmoc-Lys(Tfa)-OH
HATU, NMM
VIII
STEP H
1. Divide into 36 reactors
2. Piperidine
IX_{1-36}

Fig. 8B

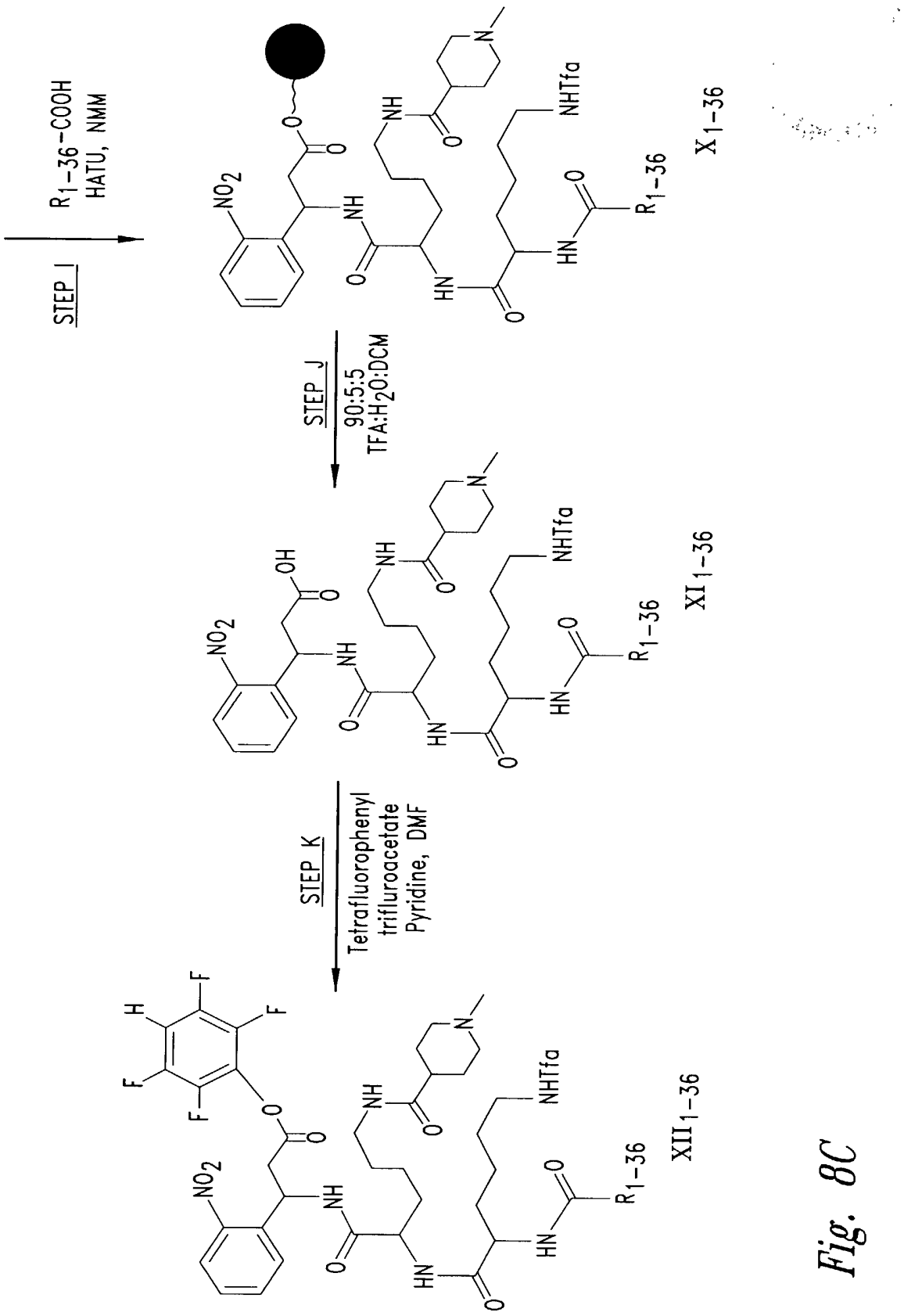
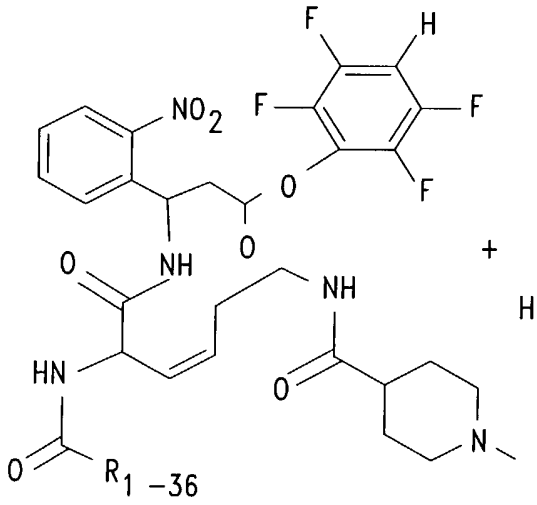
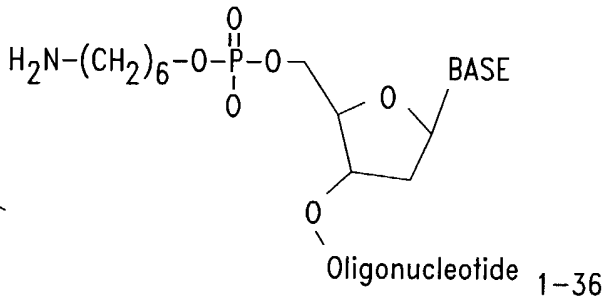

STEP I
R1-36-COOH
HATU, NMM
X1-36
STEP J
90:5:5
TFA:H2O:DCM
XI1-36
STEP K
Tetrafluorophenyl
trifluroacetate
Pyridine, DMF
XII1-36

Fig. 8C



X_{1-36}
FROM
EXAMPLE A

+

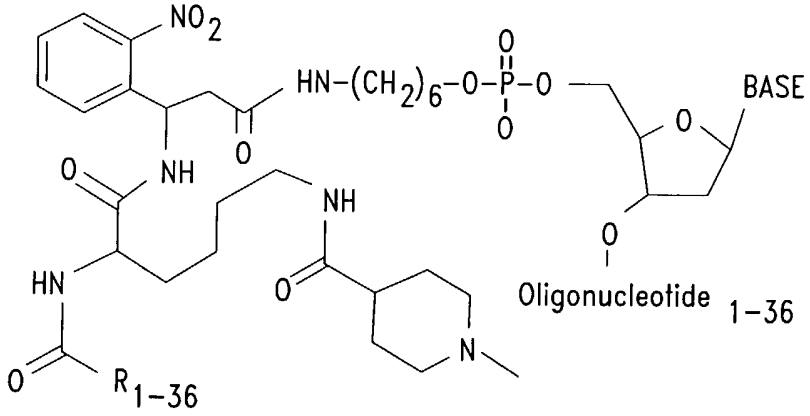


5'-Aminohexyl-tailed oligonucleotides

XI_{1-36}

STEP A

100 mM
Sodium Borate
pH 8.3



5'-CMST-Oligonucleotide Conjugate

XII_{1-36}

Fig. 9

BASE
O
O
O
O
P
O
O
H2N-(CH2)6-O-P-O
Oligonucleotide 1-36
5'-Aminohexyl-tailed oligonucleotides
XI1-36
100 mM, Sodium Borate, pH 8.3
Cyanuric chloride
STEP A
Cl
N
Cl
N
N
Cl
HN-(CH2)6-O-P-O
Oligonucleotide 1-36
XII1-36
NH2
O2N
HN
NH
R1-36
H2N
X1-36
FROM
EXAMPLE E

Fig. 10A

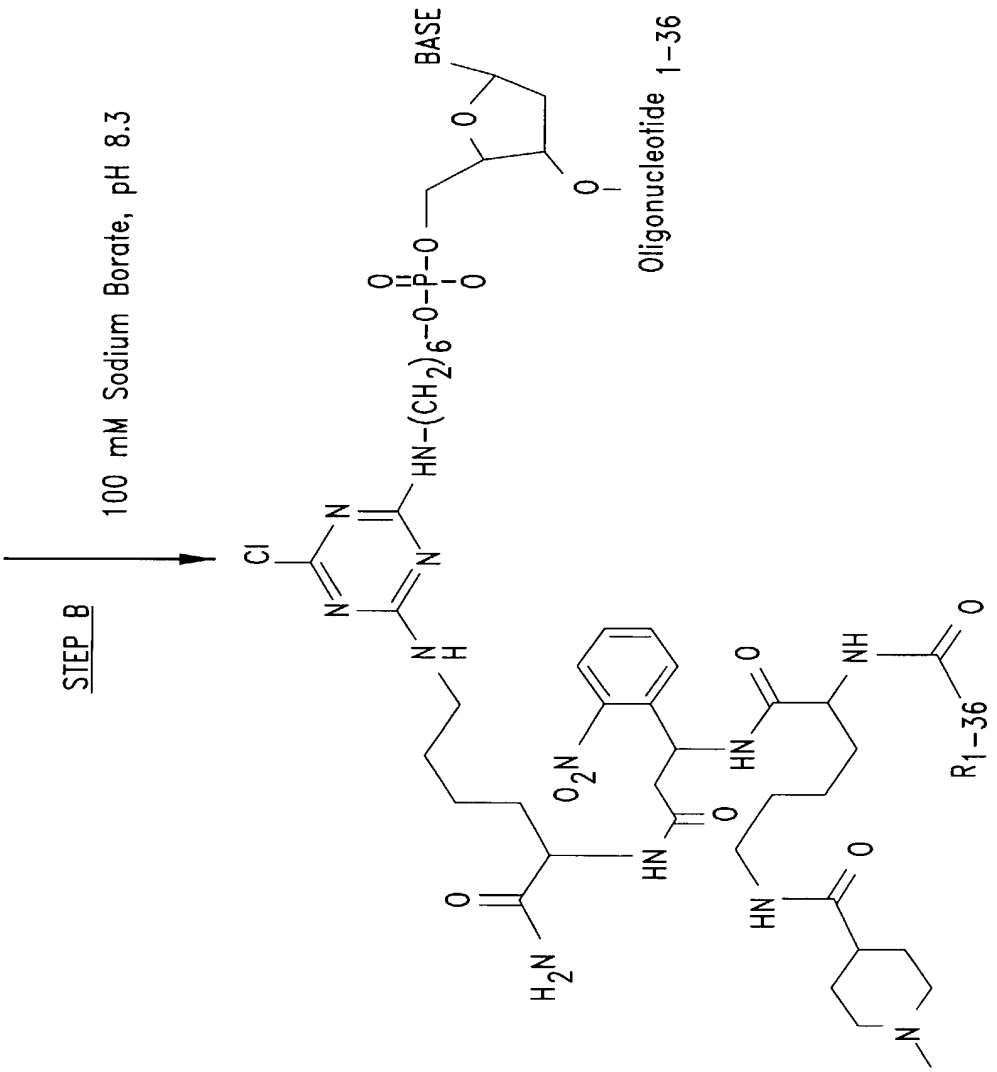

STEP B
100 mM Sodium Borate, pH 8.3
Cl
N
N
N
H
HN–(CH2)6–O–P–O
O
BASE
Oligonucleotide 1–36
O2N
HN
NH
R1–36
H2N
XIII 1–36

Fig. 10B

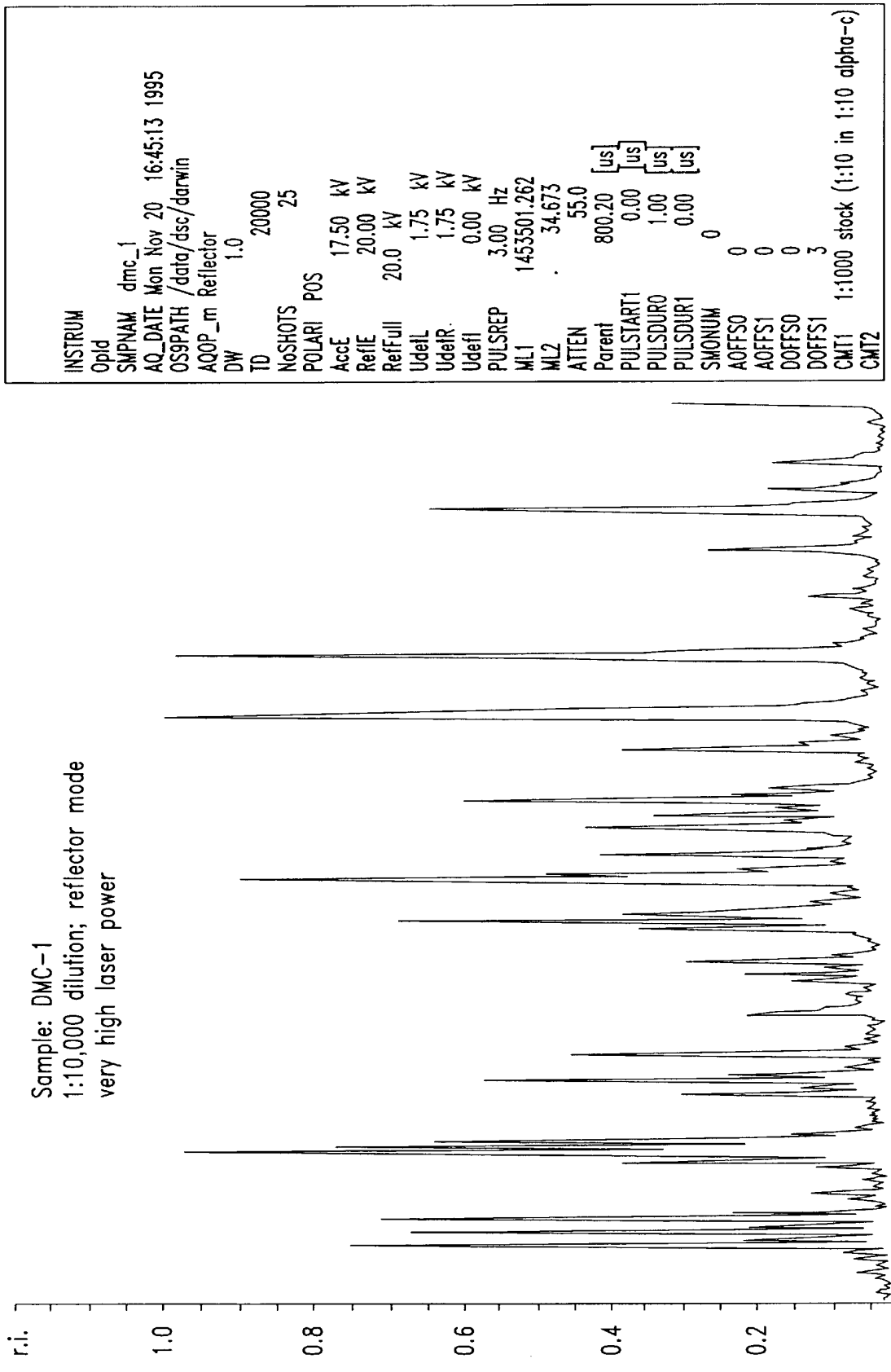

INSTRUM
Opld
SMPNAM dmc_1
AQ_DATE Mon Nov 20 16:45:13 1995
OSSPATH /data/dsc/darwin
AQOP_m Reflector
DW 1.0
TD 20000
NoSHOTS 25
POLARI POS
AccE 17.50 kV
RefIE 20.00 kV
RefFull 20.0 kV
UdelL 1.75 kV
UdelR 1.75 kV
Udel 0.00 kV
PULSREP 3.00 Hz
ML1 1453501.262
ML2 34.673
ATTEN 55.0
Parent 800.20 [us]
PULSTART1 0.00 [us]
PULSDUR0 1.00 [us]
PULSDUR1 0.00 [us]
SWONUM 0
AOFFS0 0
AOFFS1 0
DOFFS0 0
DOFFS1 3
CMT1 1:1000 stock (1:10 in 1:10 alpha-c)
CMT2
Sample: DMC-1
1:10,000 dilution; reflector mode
very high laser power
r.i.
1.0
0.8
0.6
0.4
0.2
0.0
130
150
170
190
210
230
m/z

Fig. 11

INSTRUM	
OpId	
SMPNAM	alpha_c
AQ_DATE	Mon Nov 20 14:04:49 1995
OS9PATH	/data/dsc/darwin
AQOP_m	Reflector
DW	4.0
TD	10000
NoSHOTS	25
POLARI	POS
AccE	17.50 kV
RefIE	20.00 kV
RefFull	20.0 kV
UdetL	1.75 kV
UdetR	1.70 kV
Udefl	0.00 kV
PULSREP	3.00 Hz
ML1	1454770.603
ML2	37.845
ATTEN	58.0
Parent	800.20 [us]
PULSTART1	0.00 [us]
PULSDUR0	1.00 [us]
PULSDUR1	0.00 [us]
SMONUM	0
AOFFS0	0
AOFFS1	0
DOFFS0	0
DOFFS1	3
CMT1	neat
CMT2	

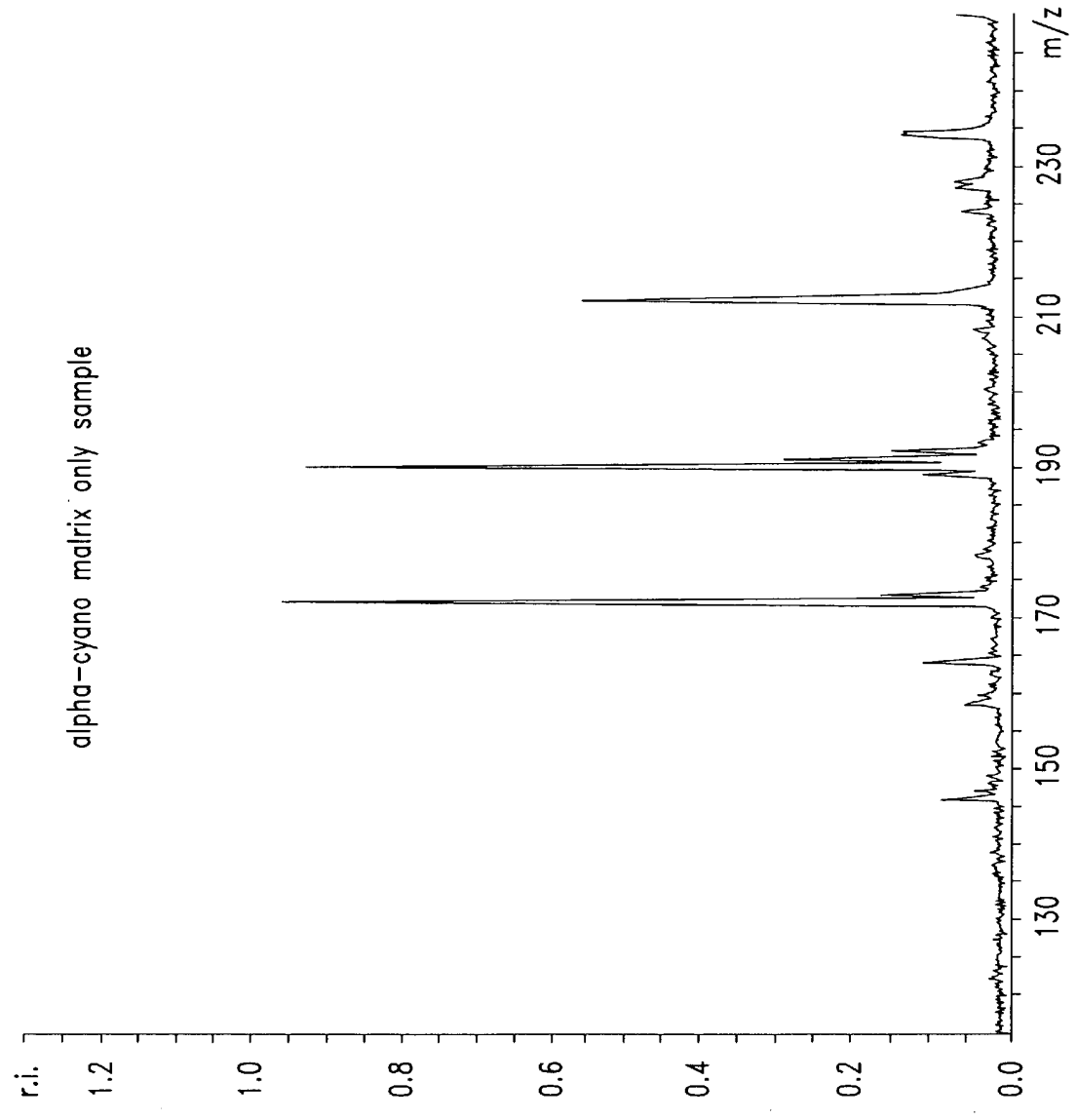


Fig. 12

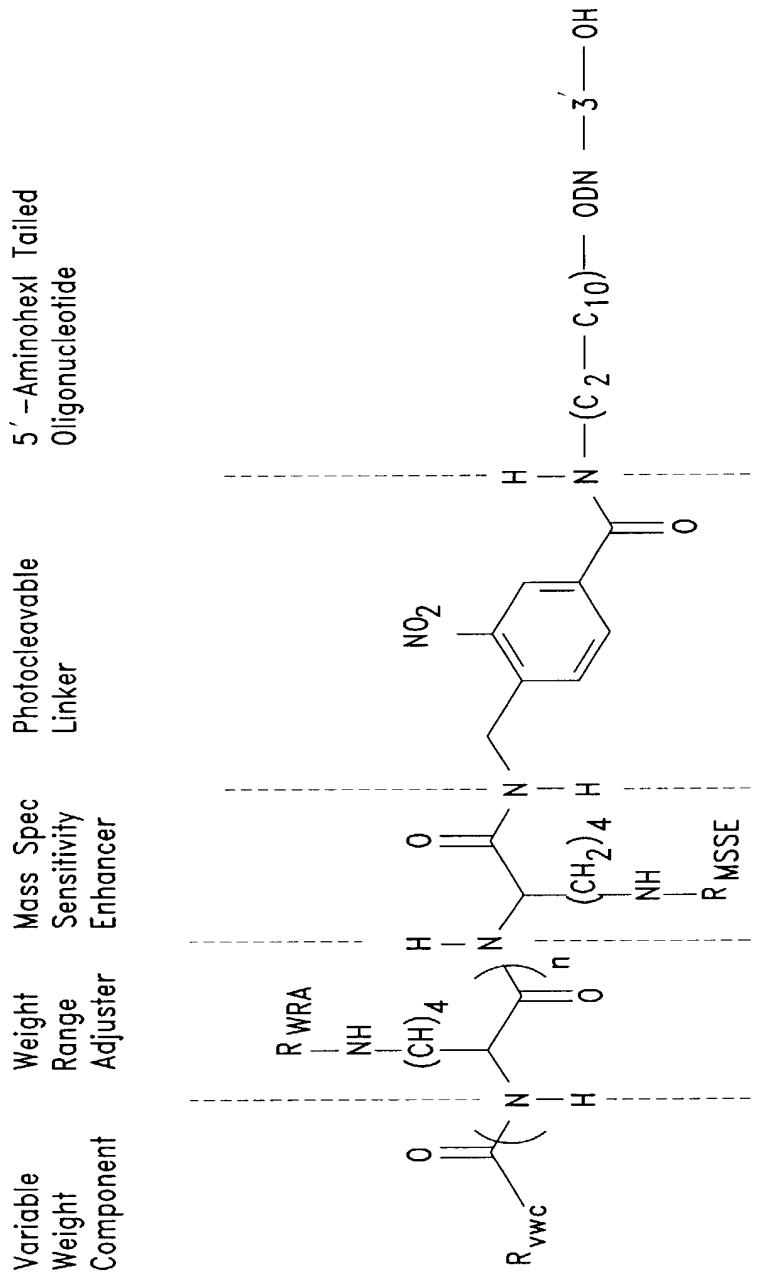

Variable Weight Component
Weight Range Adjuster
Mass Spec Sensitivity Enhancer
Photocleavable Linker
5'-Aminohexl Tailed Oligonucleotide
R vwc
R WRA
R MSSE
NO2
ODN
OH

Fig. 13

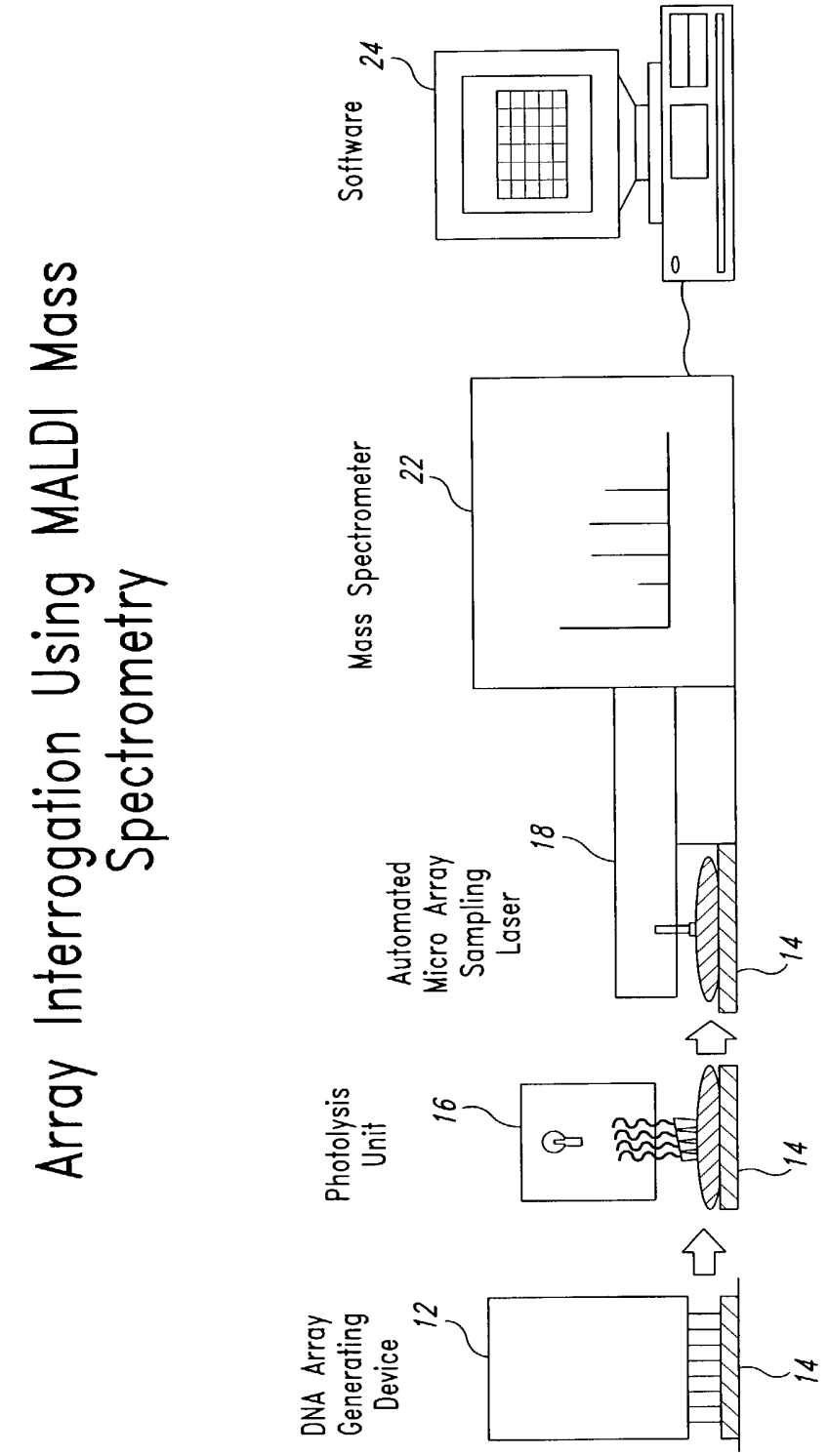

Array Interrogation Using MALDI Mass Spectrometry
Software
24
Mass Spectrometer
22
Automated Micro Array Sampling Laser
18
Photolysis Unit
16
DNA Array Generating Device
12
14

Fig. 14

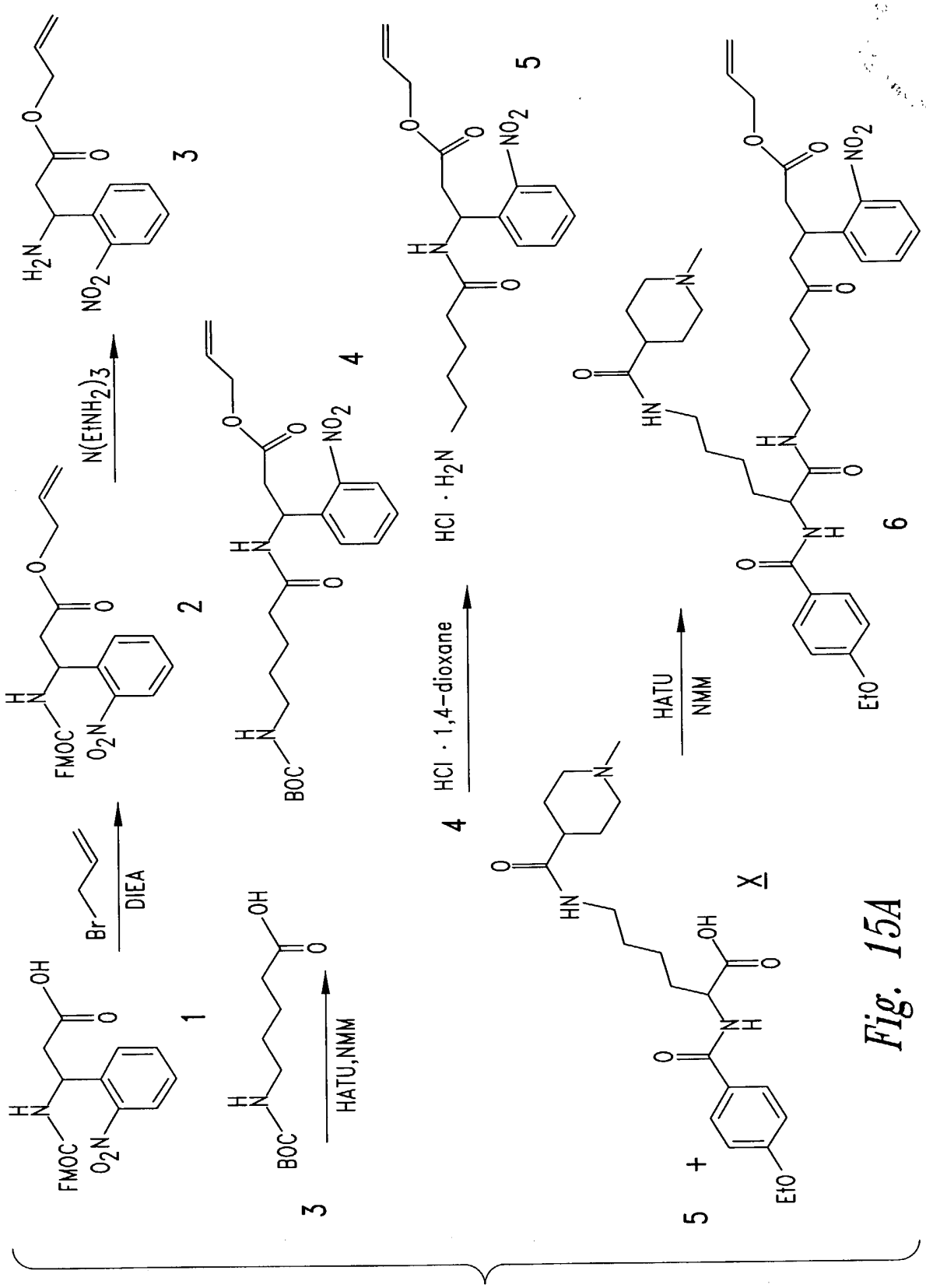

Br
DIEA
1
FMOC
O_2N
OH
HATU,NMM
3
BOC
$N(EtNH_2)_3$
2
4
NO_2
HCl · 1,4-dioxane
HCl · H_2N
5
HATU
NMM
6
EtO
X
HN
N
H
O

Fig. 15A

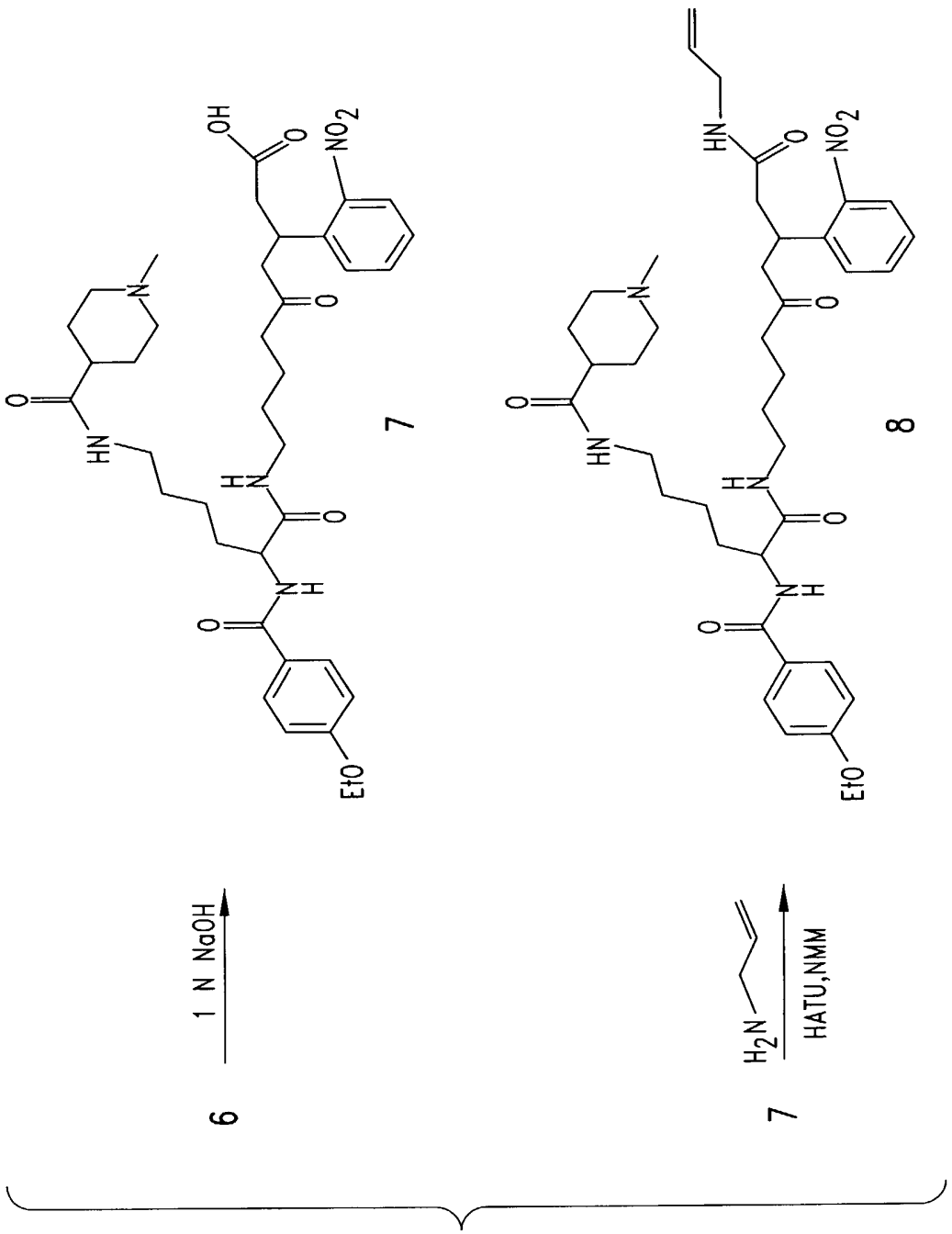


Fig. 15B

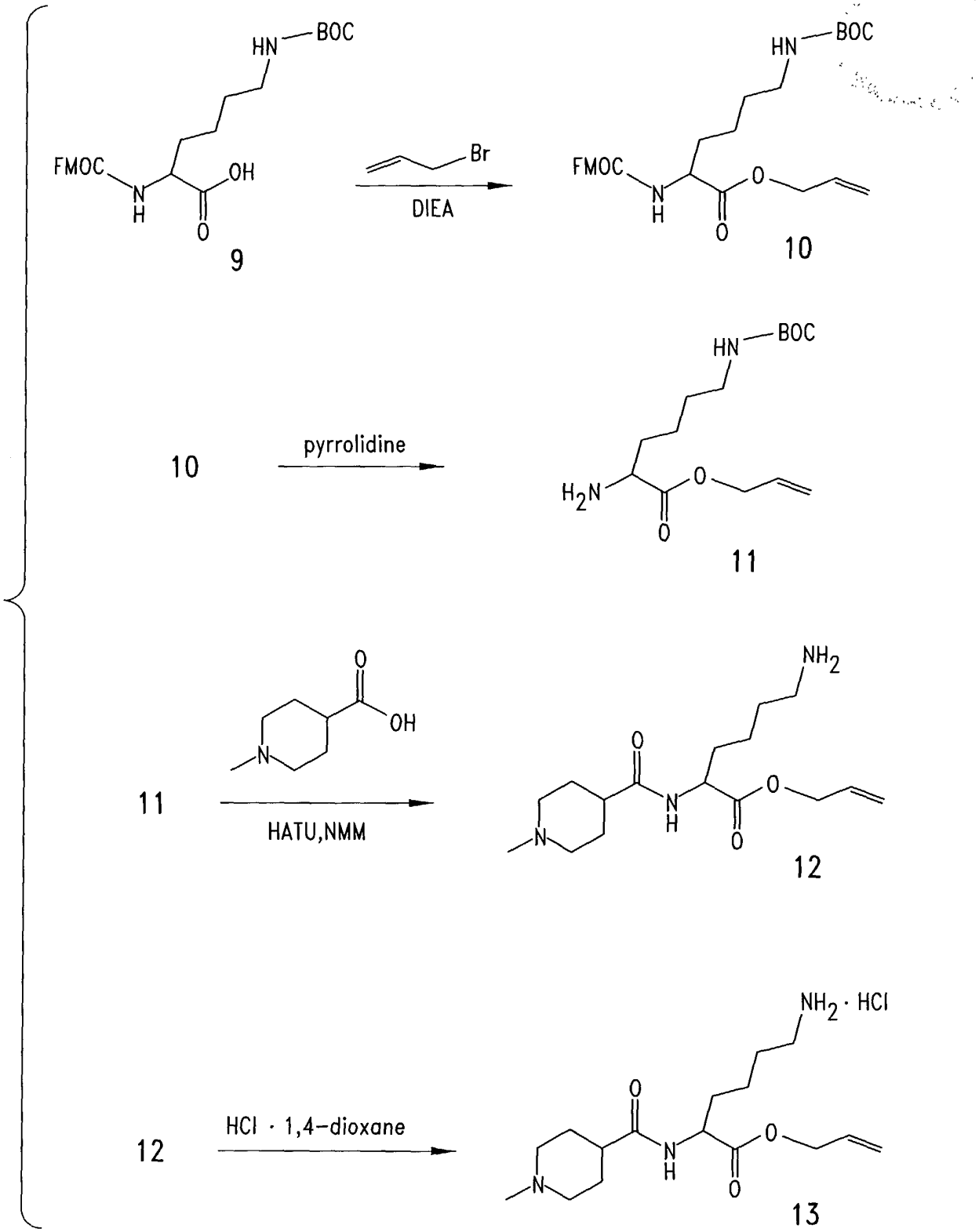

HN
BOC
FMOC
N
H
OH
O
9
Br
DIEA
10
pyrrolidine
H_2N
11
HATU,NMM
NH_2
12
HCl · 1,4-dioxane
$NH_2 \cdot HCl$
13

Fig. 16A

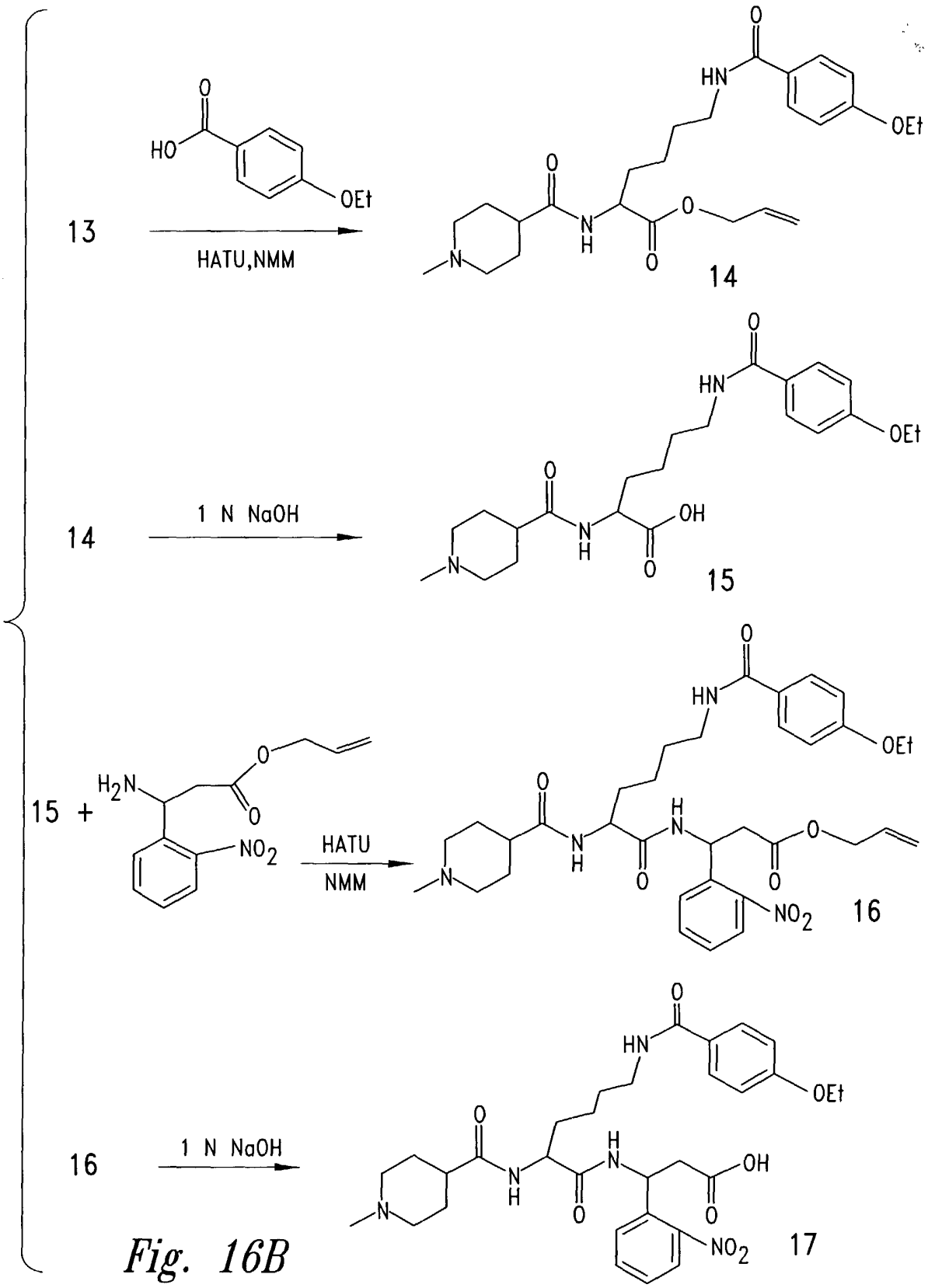


Fig. 16B

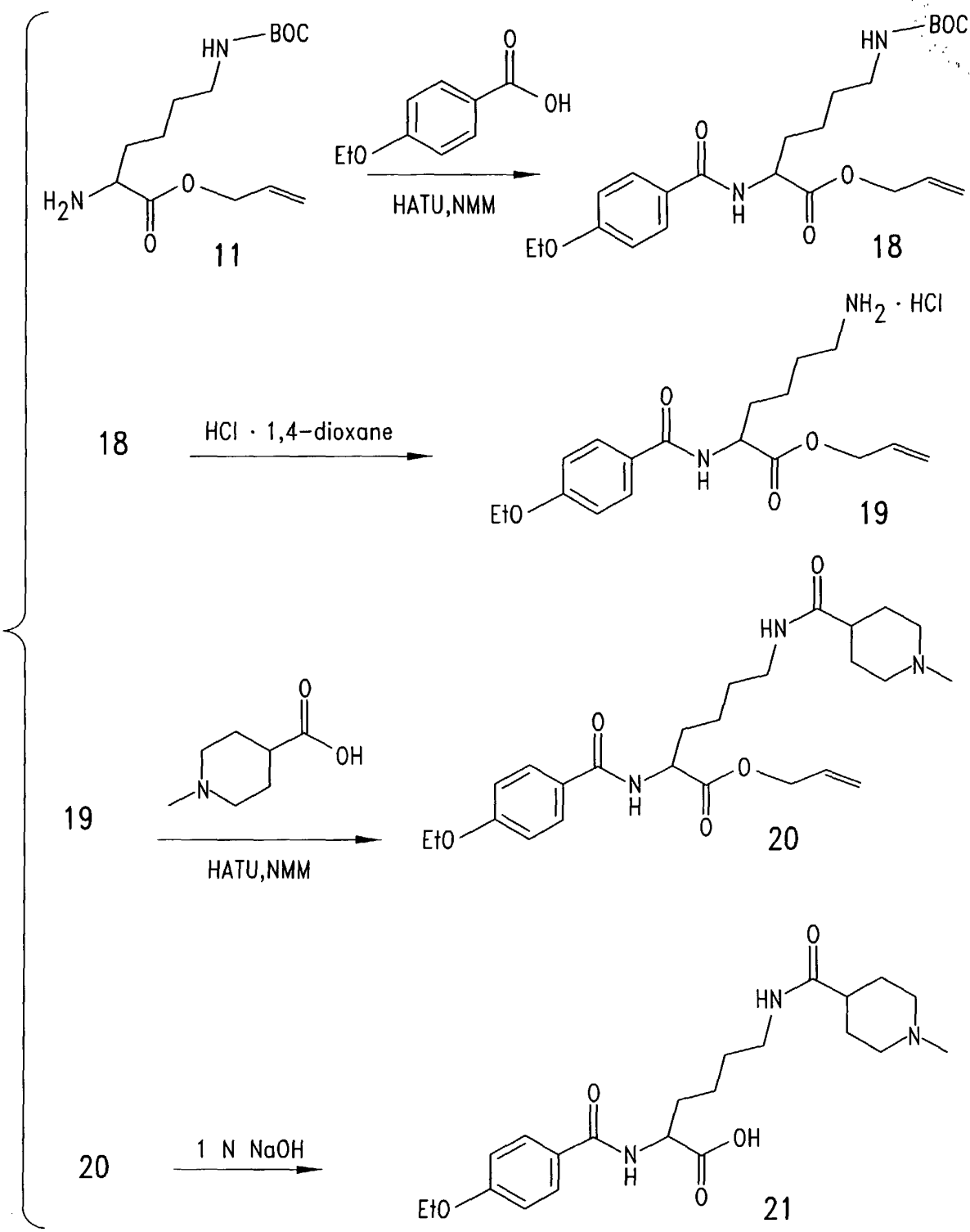

HN
BOC
H_2N
O
O
11
EtO
OH
HATU,NMM
18
$NH_2 \cdot HCl$
HCl · 1,4-dioxane
19
N
20
1 N NaOH
21

Fig. 17